

IMULATION OF THE STEADY-STATE BEHAVIOR
OF GENERAL DISTILLATION PLANTS

1979

GUIDO N ZACCHI
CI, MLM

AVHANDLING FÖR TEKNISK DOKTORSEXAMEN



DEPARTMENT
OF
CHEMICAL ENGINEERING

AVDELNINGEN FÖR KEMISK APPARATTEKNIK

LUND INSTITUTE OF TECHNOLOGY
LUND - SWEDEN





Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41553413_0025

SIMULATION OF THE STEADY-STATE BEHAVIOR
OF GENERAL DISTILLATION PLANTS

1979

GUIDO N ZACCHI
CI, MLM

AVHANDLING FÖR TEKNISK DOKTORSEXAMEN

AVHANDLINGEN KOMMER ATT FÖRSVARAS VID EN
OFFENTLIG DISPUTATION I SAL B, KEMICENTRUM,
LUND, FREDAGEN DEN 20 APRIL 1979, KL 13¹⁵.

SIMULATION OF THE STEADY-STATE BEHAVIOR
OF GENERAL DISTILLATION PLANTS

GUIDO N ZACCHI



DEPARTMENT OF CHEMICAL ENGINEERING
LUND INSTITUTE OF TECHNOLOGY
LUND
SWEDEN

DISSERTATION
APRIL 1979



Dokumentutgivare
Lund Institute of Technology
Department of Chemical Engineering
Handledare

Dokumentnamn
Dissertation
Utgivningsdatum
March 1979

Dokumentbeteckning
LUTKDH/(TKKA-1002)
/1-13/(1979)
Ärendebeteckning

Författare

Guido Zacchi

Dokumenttitel och undertitel

Simulation of the Steady-State Behavior of General Distillation Plants

Referat (sammandrag)

The optimum design of a distillation plant requires the evaluation of a wide variety of operating and design variables. This is most conveniently performed by mathematical simulation of the process. A computer program package for correlation of phase-equilibrium data and simulation of the steady-state behavior of general distillation plants is presented. The program package is capable of handling arbitrary distillation systems involving ideal as well as non-ideal physical property behavior. It has been used in the design of a distillation plant for treatment of condensate streams from a sulfite pulp mill. Different configurations were investigated to reduce energy requirements.

Referat skrivet av

G. Zacchi

Förslag till ytterligare nyckelord

Multiple towers, vapor-liquid equilibrium, modeling

Klassifikationssystem och -klass(er)

Indextermer (ange källa)

Omfång
17 pages

Övriga bibliografiska uppgifter

Språk
English

Sekretessuppgifter

ISSN

ISBN

Dokumentet kan erhållas från

Department of Chemical Engineering,
Chemical Center, P.O.B. 740,
S-220 07 Lund 7, Sweden

Pris

Mottagarens uppgifter

SIMULATION OF THE STEADY-STATE BEHAVIOR OF GENERAL DISTILLATION PLANTS

Guido Zacchi, Department of Chemical Engineering, Lund Institute of Technology, Lund, Sweden.

The thesis consists of this summary and of the following papers:

- I. Zacchi, G., Aly, G. and Jernqvist, Å.
A Computer Program for Calculating and Plotting of Liquid-Vapor Equilibria Using a Minimum of Experimental Information.
Svensk Papperstidning 80(5), 145 (1977)
- II. Zacchi, G.
DESTLA - a Computer Program for Simulation of the Steady-State Behavior of General Distillation Systems.
Report LUTKDH/(TKKA-3001)/1-41/(1978), Dept of Chem Eng, Lund Institute of Technology (1978)
- III. Zacchi, G. and Aly, G.
Simulation and Design of Distillation Units for Treatment of Sulfite Pulping Condensates to Recover Methanol and Furfural.
Part I: Incorporation with an Evaporation Unit and Use of Secondary Steam.
Accepted for publication in the *Can. J. Chem. Eng.*
- IV. Aly, G. and Zacchi, G.
Simulation and Design of Distillation Units for Treatment of Sulfite Pulping Condensates to Recover Methanol and Furfural.
Part II: Applicability of Multiple-Effect Distillation Using Live Steam.
Accepted for publication in the *Can. J. Chem. Eng.*

INTRODUCTION

Distillation represents the most widely used separation process in chemical and petroleum industries. The most common application is in the petroleum and petrochemical processes, where the distillation equipment accounts for a large portion of the capital investment. Distillation is also commonly used in the chemical process industry for purification of reactants and separation of desired products from by-products. Furthermore, an increasingly important application field is the purification of effluent streams from both chemical and other process industries, such as pulp and paper mills.

The optimum design of a distillation plant requires the evaluation of a wide variety of operating and design variables, in order to ensure not only desired product quality at minimum cost, but also to maintain this quality in cases of variation in feed composition. Different approaches may be used, such as using previously gained experience from similar plants, pilot-plant or bench-scale laboratory simulations, and mathematical simulations. The first alternative is applicable in rather few cases, apart from the petroleum industry which has access to a great amount of data on the distillation of hydrocarbons. The second alternative is rather expensive, especially if the process involves complex configurations as in extractive and azeotropic distillation.

The mathematical simulation alternative is receiving wider and wider application because it effectively enables one to study the cause-and-effect relationships between variables, exploring the effects of different operating conditions for optimization purposes, investigating the interactions of various parts of the process, and studying the effects of and the requirements for expansion projects. It is usually much cheaper and faster to conduct such studies using a mathematical model than experimentally on an operating unit. This is not to say that plant tests are not needed, since these are a vital part of confirming the validity of the model and of verifying important ideas and recommendations that result from the model simulations. Such simulations are most conveniently carried out with the aid of a computer since the calculations involved are quite extensive and of an iterative nature. It is equally important to realize that in order to obtain simulation results with reasonable engineering accuracy, access to reliable phase equilibrium data is necessary.

This thesis is concerned with the computer-aided simulation of the steady-state behavior of general distillation plants. In part I a computer program for correlation of phase-equilibrium data is presented. The main objective of that program, named EQUIL, is to compute phase-equilibria for multicomponent systems using experimental data for binary systems. In cases where there is a lack of experimental data the program makes use of a group-contribution method to predict the phase-equilibrium data.

In part II a computer program for simulation of the steady-state behavior of general distillation plants is described. The program, named DESTLA, is capable of handling arbitrary distillation systems involving ideal as well as non-ideal physical property behavior.

The application of both EQUIL and DESTLA to an industrial problem is described in parts III and IV. Both programs were used in the design of a distillation plant for treatment of condensate streams from a sulfite pulp mill. In this investigation three different configurations were studied to reduce energy requirements.

SUMMARY OF THE PRESENT WORK

PART I

Phase equilibria constitute the most important feature in the simulation of a distillation column, as it is an index of the separability of the mixture. Experimental vapor-liquid equilibrium data are available in the literature for a great number of binary mixtures, while they are quite scarce for ternary systems and nearly non-existing for mixtures containing four or more components. Since industrial distillation is rarely limited to binary mixtures, it is highly desirable that multi-component data be developed from binary data only.

In part I, a computer program, named EQUIL, for computation and plotting of vapor-liquid equilibria for binary systems as well as computation of such data for multi-component systems is presented. The equilibrium criterion used in the program is described by the following equation:

$$y_i P = \gamma_i x_i P_i^0 \quad (1)$$

where γ_i is the activity coefficient for component i in the liquid phase. The vapor pressures of pure components, P_i^0 , are calculated using the well-known Antoine's equation while the activity coefficients are obtained from one of several two-parameter models available in the program. Originally, the Van Laar, the Margules and the Wilson equations, which are described in several books^{1,2}, were included. The Wilson equation is of particular interest as it can be applied to multicomponent systems using only binary parameters. Moreover, it has been found³ to be a good compromise between simplicity and accuracy for binary and multicomponent systems. However, Wilson's equation has the undesirable feature of being inapplicable to liquid mixtures with partial miscibility. To overcome this disadvantage the more complex UNIQUAC⁴ and NRTL⁵ models were adopted in EQUIL. The former is a two-parameter model which gives the activity coefficients in terms of a combinatorial part, essentially due to differences in molecular sizes and shapes, and a residual part, essentially due to molecular interactions. The latter model is actually a three-parameter model although one of the parameters may be empirically estimated with a knowledge of the system under consideration.

The program package EQUIL, shown schematically in figure 1, has two main objectives. The first is to determine the parameters in the activity coefficient models to be used in DESTLA, a computer program for calculation of multicomponent distillation. The second objective is to plot complete equilibrium curves for binary systems. If experimental data for binary systems are available, the parameters in the activity coefficient models are evaluated by least squares minimization of a suitable objective function. Data may be fitted to either pressure, vapor-phase composition, activity coefficients or a combination of pressure and vapor-phase composition. Other objective functions, suitable for incomplete experimental data, such as dew-point data (T, P, y), are also included in the program.

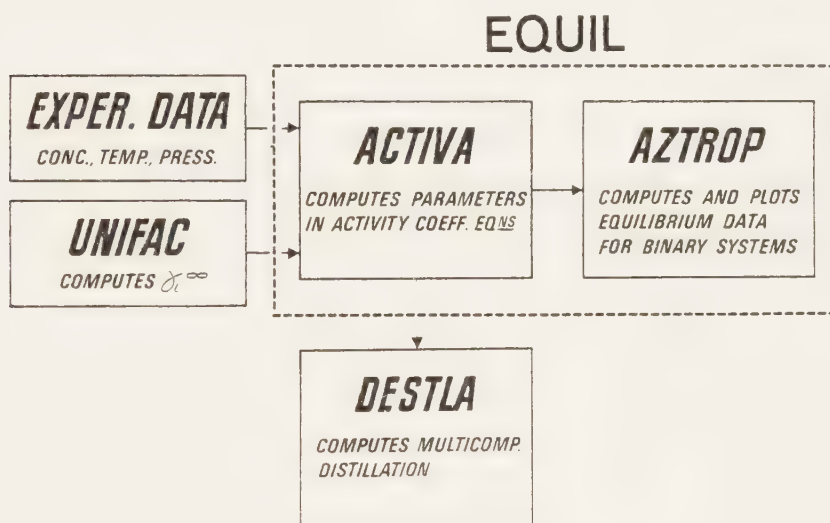


Figure 1. Schematic flow diagram of EQUIL

In the absence of experimental data for a given system, a group-contribution method, the UNIFAC model⁶, for predicting activity coefficients in nonelectrolyte liquid mixtures is used. The basic concept of the UNIFAC model is that a liquid mixture can be looked upon as a solution of a relatively small number of functional groups, such as $-\text{CH}_3$, $-\text{CHO}$, CHCl_2 etc. The UNIFAC model is used in EQUIL to predict the activity coefficients at infinite dilution which are then used to obtain the parameters in the activity coefficient models.

The computer program AZTROP calculates and plots both isobaric and isothermal equilibrium curves for binary systems. The input data required

consist mainly of Antoine's constants for the pure components and the parameters for calculating activity coefficients according to one of the previously mentioned models. AZTROP computes bubble- and dew-point temperatures or pressures, equilibrium vapor compositions, activity coefficients and relative volatilities for different liquid compositions. This data is printed out in a tabulated form and may also be plotted. The output will also contain information on whether the system has an azeotrope and if partial liquid miscibility occurs.

EQUIL comprises about 2300 punch cards and is divided into 15 sub-programs including both minimization and plotting routines. It requires about 21 400 words of core memory. The CPU-time consumption for this program package to compute and plot complete vapor-liquid equilibrium information for a binary system is about 8 seconds in CPU-time and 11 minutes of plotting.

Four numerical examples are presented in order to illustrate the flexibility and ability of EQUIL. It is shown to be a suitable tool for the design engineer to compute and plot vapor-liquid equilibrium, using only a few experimental data points, with an acceptable engineering accuracy. It allows the calculation of equilibrium information for a given system at some temperature or pressure value different from that at which experimental data are available. When no experimental data are available, the UNIFAC model may be used to predict vapor-liquid equilibria. A given multicomponent system contains a number of constituent binary systems. In many cases, experimental activity coefficients may be available for some, but not all, of these binaries. UNIFAC may be used here to predict the activity coefficients for each of the components in the unknown binaries. These predicted activity coefficients can then be used to compute Wilson, UNIQUAC or NRTL parameters which in turn allow the calculation of vapor-liquid equilibria for multicomponent systems.

The program has recently been extended in order to account for vapor-phase non-ideality by including the vapor-phase fugacity coefficient, ϕ_i , in the equilibrium criterion described by equation (1). The fugacity coefficient in EQUIL can be calculated either with the method of Hayden and O'Connell⁷ or the method of O'Connell and Prausnitz⁸.

PART II

The importance of distillation as a chemical engineering unit operation has resulted in much work being done to simulate the behavior of such units. The mass and heat balances modeling a multicomponent distillation system operating at steady-state are highly non-linear and interdependent. Hence, the rigorous solution to such problems requires an enormous load of repetitive calculations which are most conveniently performed with the aid of a computer. The modern high-speed, large-storage computers have made it possible to use algorithms or iteration methods which are oriented to the solution of general distillation problems, involving non-ideal mixtures and interlinked complex column configurations. An example of such a computer program is the recently presented MULTICOL⁹ system.

The current trend is to consider the distillation columns as a part of a chemical process, solving the heat and mass balances for the overall process with a flowsheeting program. A number of such programs are in use today¹⁰, mainly in large companies.

The main goal of this work was to develop a computer program, DESTLA, for simulation of the steady-state behavior of general multicomponent distillation systems. It is a part of a larger research project, started in 1971 at the department of Chemical Engineering, Lund Institute of Technology, concerning the simulation of various chemical engineering unit operations. The first result from that project was the computer program INDUNS¹¹, for design and evaluation of general multiple effect evaporation plants. The program uses a modular approach to flowsheeting, based on the ideas of Jernqvist et al¹² who used a so called "unit cell" and a "connection matrix" for the description of the plant flow sheet.

The same ideas are used in DESTLA, which is based on a modular approach to both flowsheeting and thermodynamics. The unit cell of DESTLA, shown in figure 2 below, consists of a plate, a flasher, a reboiler, a partial condenser, a total condenser, a heat exchanger, a mixing vessel for liquids, a mixing vessel for vapors and a liquid separation vessel. Flow sheets of arbitrary complexity may easily be assembled by specifying the destination and source of all streams connecting two pieces of equipment. Furthermore, the flexibility is increased by the modular approach to thermodynamics which allows the user to choose between the

models for phase-equilibria and enthalpy available in the program or to replace them with self-supplied models.

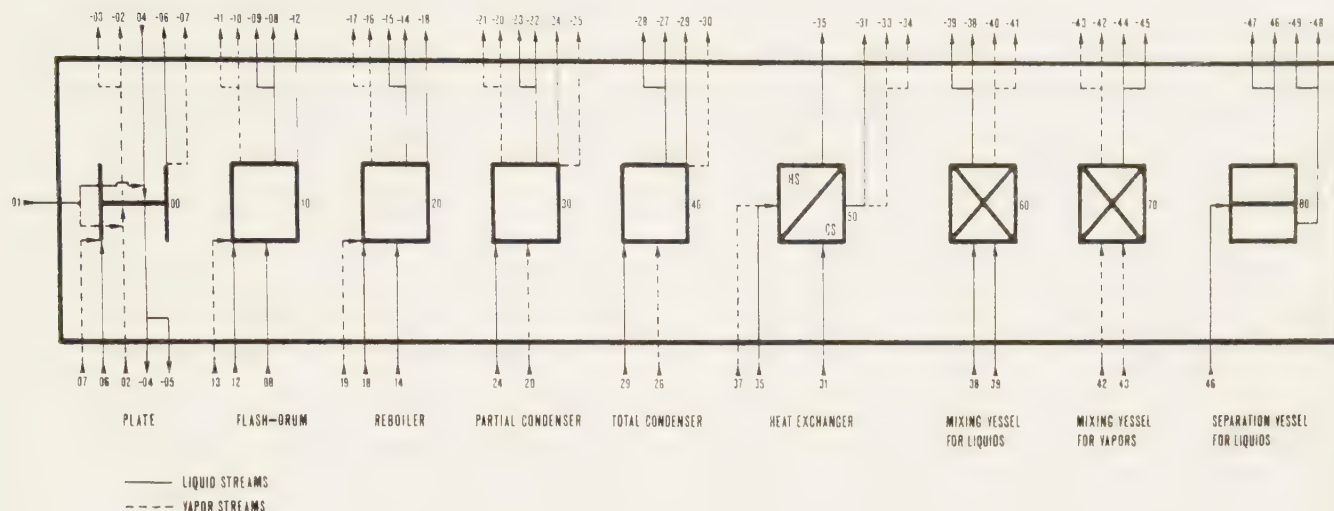


Figure 2. The unit cell of DESTLA

Plates, flash-drums, reboilers and partial condensers are all treated as ideal stages, yielding a vapor and a liquid outlet stream at equilibrium. However, real plates, which accounts for mass transfer efficiencies, can be simulated using a Murphree plate efficiency.

As can be seen from the unit cell configuration, the flow input to a plate consists of a vapor, a liquid and a feed stream. The latter is assumed to mix perfectly with the other entering streams. Split streams are allowed, in order to simulate intermediate vapor and liquid withdrawals from the column.

All pieces of equipment in the unit cell configuration, except for mixing and separation vessels, can either be heated or cooled. The heat transfer may be specified either explicitly or as a heating/cooling stream. Such streams are symbolized, as shown in the unit cell, such that they enter the unit at the left-hand lower corner and leave at the right-hand upper corner, with the exception of the heat exchanger. Moreover, side streams can be withdrawn from the majority of the equipment involved in the unit cell.

The main phases of the executive program DESTLA are; input of data, input data testing, unit cell calculations and output of data. Input data consists mainly of the flow sheet, described by specifying the

destination and origin of all streams connecting two pieces of equipment, phase-equilibria and enthalpy data, heat transfer data and special data such as Murphree plate efficiencies, pressure drop across a plate, reflux ratios and degree of subcooling in total condensers. Furthermore, flow rate and properties for all incoming external streams not originating from other pieces of equipment within the flow sheet must be specified.

A comprehensive test of all input data is then performed in order to avoid absurd or incomplete data. About 50 self-explanatory error messages together with echoed input data facilitate error detection. If no errors are detected, the calculation phase is initiated. Mass and heat balances modeling the various unit operation modules are solved using a plate-to-plate computational procedure. This method is based on mass and energy conservation envelopes encircling single stages and using only entering streams in the calculation of outlet streams. In order to accelerate convergence, the temperatures on equilibrium stages are calculated with the aid of ADJUST, an adaptive convergence algorithm for general trial and error computations¹³. In the output data phase all important information, both computed and provided as input data, is printed out in fully written out text.

The abilities of the computer program are demonstrated by solving four test examples. These show DESTLA's capability of handling a wide variety of normally difficult distillation calculations, such as multiple column configurations, superfractionation, i.e. separation of components of nearly the same volatility, and problems involving strongly non-ideal mixtures. A problem related to distillation of wide-boiling mixtures is also solved, after a slight modification of the solution method. Furthermore, the program was applied to solve problems concerning the separation of homogeneous and heterogeneous azeotropic systems^{14,15}.

PARTS III - IV

Water pollution, due to effluent streams from both chemical and other process industries, is a very real problem. Environmental as well as economical aspects, i.e. losses of chemicals, necessitate an increased treatment of such streams. This may be performed by different separation processes such as distillation, adsorption, liquid extraction and biological treatment. The aim of this work was to investigate the potential of distillation for treatment of the condensate effluent from a bisulfite pulping mill, using the previously described computer programs EQUIL and DESTLA. This investigation was carried out in cooperation with Nymölla AB which supplied the necessary stream data.

The study was based on cooking and evaporation condensates with a flow rate of 73 ton/h and containing 2.1 g/l of methanol and 1.6 g/l of furfural. These chemicals were to be recovered and other by-products, such as acetic acid, sulfur dioxide and p-cymene, were not considered.

Vapor-liquid and liquid-liquid equilibrium data for the ternary system were computed with EQUIL using experimental data for the three binaries involved. Both the Wilson and the UNIQUAC models, for calculation of liquid-phase activity coefficients, were used. The water-furfural system has a heterogeneous azeotrope and this was accurately predicted using the latter model. The Wilson equation was used for computation of the vapor-liquid equilibria in the distillation columns, thus neglecting eventual phase-splitting while the UNIQUAC model was used for computation of the liquid-liquid separation in the liquid decanter.

It was decided to perform the fractionation in three steps. The first step involves stripping of the volatile organics and is followed by two upgrading steps, for methanol and furfural respectively. Rather than examining just the distillation process as such, the primary emphasis has been focused on economising the energy requirements, since the operating cost plays an important role in determining the profitability of the entire process. Three design alternatives, which differ mainly in energy supply to both stripper and methanol columns were studied. The first two alternatives use the principle of multiple effect distillation. In the third alternative the stripper is incorporated into the evaporation unit of the mill.

A schematic flow sheet for one of the design alternatives is shown in figure 3 below. In this alternative, two strippers are operated in parallel on the liquid side and in series on the vapor side. The feed F is split more or less equally among the two strippers and is separated into relatively pure bottoms, streams $B1A$ and $B1B$, and overhead products, streams $D1A$ and $D1B$, somewhat enriched in methanol and furfural. The latter streams are pumped into the methanol column, which separates them into nearly pure methanol, stream $D2$, and nearly pure condensate, stream $B2$. A liquid side stream containing a high furfural concentration is withdrawn and sent to the liquid separation vessel after being subcooled. This two-phase mixture is separated and the water-rich layer is refluxed to the methanol column while the furfural-rich layer is fed to the top plate of the furfural column. Nearly pure furfural is taken out as bottom $B3$ while the overhead vapor, $V3$, is condensed and recycled to the separation vessel.

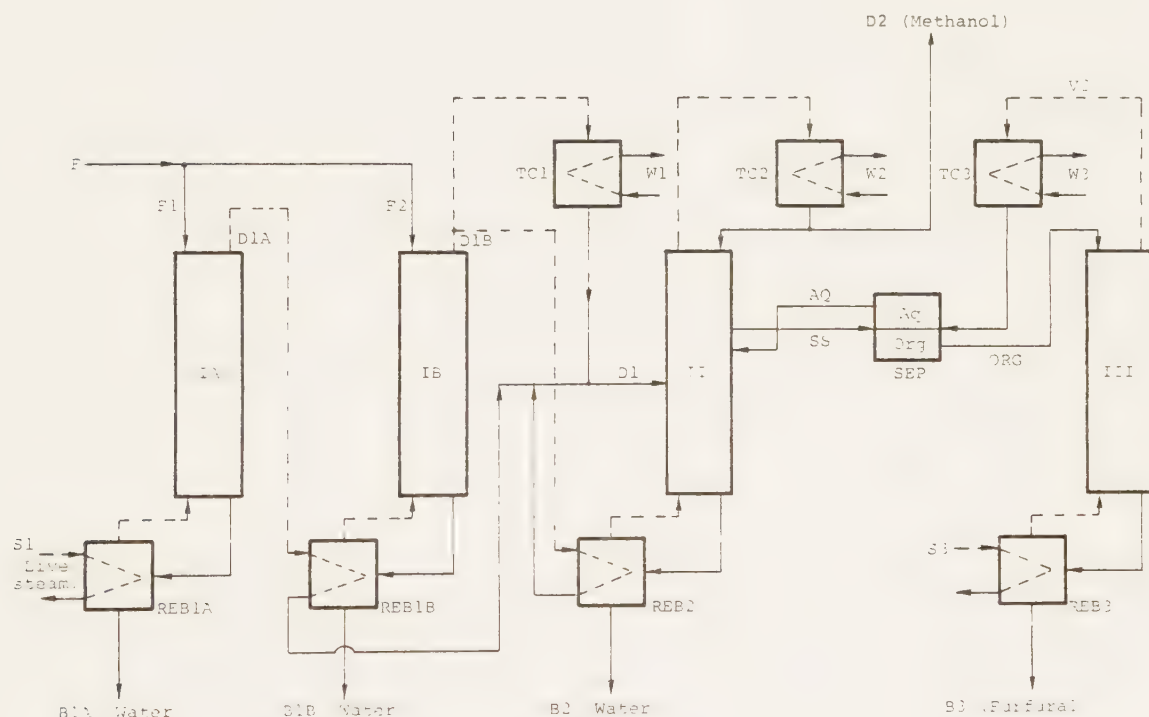


Figure 3. Schematic flowsheet for the two-stripper configuration

The first stripper and the furfural column use live steam as the energy source in their reboilers while the second stripper and the methanol column uses the overhead vapor from the first and second stripper respectively. Excess low-pressure vapor is bled off from

the top of the second stripper and is condensed in TC1, which was designed to preheat steam condensate returning to the reboiler, stream W1.

The other multiple effect distillation alternative uses only one stripper and thus requires almost twice the energy input, albeit producing much more low-pressure steam to be used for other purposes in the mill, compared to the two-stripper configuration.

The third design alternative uses secondary steam as energy source by incorporating the stripper in the evaporation unit. The upgrading of the methanol and furfural products is similar for all alternatives.

The three configurations were simulated using DESTLA, which delivered all important data, such as flow rate, composition, temperature, and heat content of the streams leaving each piece of equipment involved in the distillation plant. The primary strippers were simulated separately while the methanol and furfural columns were simulated as one unit since both columns have a liquid separation vessel in common. Optimal feed plate location and the relationship between number of ideal plates and energy requirements were also investigated for the various columns, by repeated execution of DESTLA. Some runs were carried out specifically to determine the appropriate feed split for the two-stripper configuration. Furthermore, several runs were carried out with different locations of the side-stream, SS, and reflux stream, AQ, to investigate the influence on the methanol and furfural concentration profiles. In the above simulations most of the equipment available in the unit cell of DESTLA is involved.

An economic analyses of the three design alternatives was performed. This resulted in nearly the same capital cost, about 6 MCr, for all alternatives. The incorporation alternative was found to be the most profitable with a pay-off period of 2.3 years. However, creation of a bottleneck in the washing cycle of the evaporation plant and complexity of the control design needed for such an incorporation are disadvantages associated with this alternative. The other design alternatives have approximately the same pay-off period, about 3 years, when a full price is charged for the excess low-pressure steam produced. On the other hand if this excess steam can not be used for tasks that otherwise would require live steam, the pay-off period for the one-stripper configuration will considerably

increase while the profitability of the two-stripper alternative will remain almost unaltered.

A summary of parts III and IV was presented at the third International Symposium on Distillation¹⁵ held in London in April 1979.

FUTURE WORK

Based on the experience gained in developing the computer system presented in this work some possible extensions may be made. In order to decrease the computation time for problems involving strongly non-ideal systems, the computation procedure in DESTLA may be modified both by decreasing the number of vapor-liquid equilibrium calculations and by introducing an adequate method to accelerate convergence. The system may also be extended to cope with problems involving parametric searches. This will be possible by modifying the input and output procedures in order to store the result from a steady-state simulation and use it as a starting point for the next calculation. Thus if the various parameters which are to be studied have not greatly altered, the new steady-state solution may be obtained in relatively few iterations. The same procedure may also be used to investigate the optimal feed plate location in a specific distillation column. This approach has already been applied to a simple distillation column with satisfactory result.

Another possible extension is to incorporate a mathematical model for calculation of the Murphree plate efficiency. However, this extension may be regarded pointless as long as there is no significant improvement of the early AIChE model¹⁶.

The computer program DESTLA is constructed in a way that easily allows its linkage to similar programs for other unit operations. There are plans within the Department to link DESTLA to a program for simulation of extraction processes, which will be developed in the very near future. To start with, both programs will be used to modify the condensate treatment plant, presented in parts III and IV of this thesis, in order to include acetic acid recovery, a by-product which was disregarded earlier.

Future development of the computer program EQUIL will probably be focused on incorporating improved correlation and prediction models for liquid-phase activity coefficients since a continuation of research work within this field is expected.

ACKNOWLEDGEMENTS

This work was carried out at the Department of Chemical Engineering, Lund Institute of Technology, during the years 1973-1978, and was partly financed by the Swedish Board for Technical Development.

I express my sincere gratitude to Professor Åke Jernqvist for his introduction to the field of multicomponent distillation and for his great optimism and encouraging support throughout the course of this work. During his 3-years leave to industry, the necessary support was given by Acting Professor Gharib Aly to whom I am especially grateful for valuable assistance and constructive discussions.

I wish to thank Professor Aage Fredenslund at Institutet for Kemiteknik, The Technical University of Denmark for his valuable assistance and stimulating discussions in the first part of this work.

Nymölla AB is gratefully acknowledged for their cooperation and kind permission to publish the results obtained in parts III and IV of this work.

Many thanks to my colleagues at the Department of Chemical Engineering for valuable collaboration. Many thanks are also due to Mr Hans-Olof Jönsson, for skilful drawings, and to Mrs. Sonja Dahlström for the excellent typing of all my manuscripts.

REFERENCES

1. Prausnitz, J.M., "Molecular thermodynamics of fluid-phase equilibria", Prentice-Hall, Englewood Cliffs N.J. (1969)
2. Null, H.R., "Phase equilibrium in process design", Wiley-Interscience, New York (1970)
3. Orye, R.V. and Prausnitz, J.M., Ind. Eng. Chem. 1965, 57, 18
4. Abrams, D.S. and Prausnitz, J.M., AIChE J., 1975, 21(1), 116
5. Renon, H. and Prausnitz, J.M., AIChE J., 1968, 14(1), 135
6. Fredenslund, A., Jones, L.R. and Prausnitz, J.M., AIChE J., 1975, 21, 1086
7. Hayden, J.G. and O'Connell, J.P., Ind. Eng. Chem. Proc. Des. Dev., 1975, 14(3), 209
8. O'Connell, J.P. and Prausnitz, J.M., Ind. Eng. Chem. Proc. Des. Dev., 1967, 6(2), 245
9. Winter, P. and Matthew, I., Processing 1976 (July), 11
10. Flower, J.R. and Whitehead, B.D., "Computer-aided design: A survey of flowsheeting programs", Chem. Eng. 1973, 271
11. Bolmstedt, U. and Jernqvist, Å., Computer aided design 1976, 8, 142
12. Jernqvist, Å. Olgård, G. and Hedström, B., 1966, 69(15), 477
13. Jernqvist, Å. "ADJUST - an adaptive convergence algorithm for general trial and error computations", Dept. of Chem. Eng., Lund Institute of Technology, Report no. 75-F-1 (1975)
14. Zacchi, G. "DESTLA - user's manual", Dept. of Chem. Eng., Lund Institute of Technology, LUTKDH/(TKKA-3001)/1-30/(1978)
15. Zacchi, G. and Aly, G. "Applicability of some energy-saving techniques in a distillation process for treatment of sulfite pulping condensates and economic by-product recovery", presented at the third international symposium on distillation, London (1979)
16. AIChE, "Bubble - Tray Design Manual", New York (1958)

A computer program for calculating and plotting of liquid-vapor equilibria using a minimum of experimental information

GUIDO ZACCHI, GHARIB ALY and ÅKE JERNQVIST

A computer program for calculating and plotting of liquid-vapor equilibria using a minimum of experimental information

GUIDO ZACCHI, GHARIB ALY and ÅKE JERNQVIST, Department of Chemical Engineering, Lund Institute of Technology, Lund

KEYWORDS: Distillation, Process columns, Design, Computer programs, Vapor liquid equilibrium^{*}, Activity coefficient, Azeotropes.

SUMMARY: A computer program package for computation and plotting of vapor-liquid equilibria necessary for distillation tower design calculations has been developed at the Department of Chemical Engineering, Lund Institute of Technology. The program package, named EQUIL, requires a minimum of supporting experimental equilibrium data. However, if there are experimental data available for a given set of conditions, EQUIL computes and plots complete equilibrium information for another set of conditions which may be required for design calculations. In the cases where no experimental data are available, the recently developed UNIFAC model accurately predicts vapor-liquid equilibrium compositions using parameters which reflect chemical and physical interactions between functional groups.

Four numerical examples are presented in this work to illustrate the flexibility and applicability of this program package. A combination between EQUIL and DESTLA, a computer program for calculation of general multicomponent distillation systems, is also illustrated.

Five different diagrams, describing equilibrium information for a given binary system, can be plotted in a flexible way as requested by the user. The CPU-time consumption for EQUIL to compute such information for one system using 15 experimental data points is about 2 seconds.

□ Ett datorprogram för beräkning och plottning av ånga—vätska jämvikter, erforderligt vid dimensionering av destillationskolonner, har utvecklats vid Avdelningen för Kemisk Apparatteknik, Tekniska Högskolan i Lund. Datorprogrammet, EQUIL, kräver ett minimum av experimentella jämviktsdata. Om det finns experimentella data tillgängliga vid ett visst tillstånd, beräknar och plottar EQUIL fullständiga jämviktssamband vid ett annat, för dimensionering önskat, tillstånd. I de fall då experimentella data ej finns tillgängliga, uppskattas jämviktskurvan med UNIFAC-modellen, en nyligen utvecklad metod som använder parametrar baserade på kemiska och fysikaliska interaktioner mellan funktionella grupper.

Fyra numeriska exempel presenteras i detta arbete för att illustrera flexibiliteten och tillämpningsmöjligheterna av detta datorprogram. En kombination av EQUIL och DESTLA, ett datorprogram för beräkning av generella destillationsanläggningar, visas också.

Fem olika diagram, vilka ger information om ånga—vätska jämvikten för ett givet binärt system, kan plottas enligt användarens önskemål på ett flexibelt sätt. För beräkningen av sådan information för ett system omfattande femton experimentella datapunkter förbrukar EQUIL cirka 2 sekunder i CPU-tid.

□ Im Institut für chemische Verfahrenstechnik der Technischen Hochschule in Lund wurde ein Computerprogramm für die Berechnung und Auftragung von Dampf-Flüssigkeitsgleichgewichten, die für die Berechnung von Destillationskolonnen erforderlich sind, entwickelt. Das Programm, als EQUIL bezeichnet, erfordert ein Minimum von experimentellen Gleichgewichtsdaten. Wenn experimentelle Daten für gewisse Bedingungen vorhanden sind, dann kann EQUIL komplette Gleichgewichtsdaten für einen Satz anderer Bedingungen berechnen und auftragen. Wenn keine experimentelle Daten zur Verfügung stehen, dann werden Gleichgewichtsdaten mit Hilfe des UNIFAC-Modelles, einer letzthin entwickelten Methode, die sich auf chemische und physikalische Parameter gründet, geschätzt.

In dieser Arbeit werden vier numerische Beispiele präsentiert, um die Flexibilität und die Anwendungsmöglichkeit dieses Computerprogrammes zu demonstrieren. Eine Kombination von EQUIL und DESTLA, eines Computerprogrammes für die Berechnung von generellen Destillationsanlagen, wird ebenfalls aufgezeigt.

Fünf verschiedene Diagramme, die über Dampf-Flüssig-

keitsgleichgewichte für ein gegebenes binäres System informieren, können den Wünschen des Anwenders auf eine flexible Weise angepasst aufgetragen werden. Für die Berechnung so einer Information für ein System mit 15 experimentellen Punkten verbraucht EQUIL ca 2 Sekunden CPU-Zeit.

ADDRESS OF THE AUTHORS: Lunds Tekniska Högskola, Box 740, S-220 07 Lund 7, Sweden.

The success or failure of most separation processes depends on a favorable equilibrium relationship between the phases to be separated. In the past the chemical engineer has usually relied on expensive laboratory data, or on the oversimplified ideal-solution concept, or on the assumption of constant separation factors as a basis for design calculations. Since it is often not possible to make all the measurements necessary for a complete description of the desired equilibria, some less reliable assumptions have been used extensively in industrial design. However, it is often possible today to arrive at a quantitative description of the phase equilibria involved in a given practical problem with a minimum of supporting experimental data. This description is often sufficiently accurate for the design engineer.

While some experimental vapor-liquid equilibrium data for binary mixtures are available in the literature, they are quite scarce for ternary systems and nearly nonexistent for mixtures containing four or more components. Since industrial separation operations are rarely limited to binary mixtures, it is highly desirable that multicomponent data be developed from binary data only.

For a binary system which is assumed to be ideal, the vapor-liquid equilibrium composition data may be calculated from the vapor pressure-temperature data of the pure components at and around atmospheric pressure. For systems known to be approximately ideal, the use of such data may be satisfactory within the limits of engineering accuracy. However, the greater majority of systems encountered in practice are nonideal in either of or both the vapor and liquid phases. Furthermore, the increasing use of rigorous design techniques for separation equipment has produced a need for reasonably accurate vapor-liquid equilibrium composition data. Optimization of operating conditions and closer integration of equipment have enhanced this need.

It is the purpose of this work to present a flexible digital computer program, EQUIL, which computes and plots the vapor-liquid equilibrium data for binary systems. In addition to a minimum of experimental data the program requires input information such as the Antoine constants for the pure components, the pressure or temperature at which the equilibrium data will be computed, and which information should be plotted. If no experimental data are available for a binary system, a recently developed group-contribution method, the UNIFAC model, can be used to predict the activity coefficients of the system. The parameters obtained for binary systems can then be used for calculating vapor-liquid equilibria for multicomponent systems.

Basic equations

For a nonideal gas mixture the fugacity coefficient ϕ_i relates the vapor-phase fugacity f_i^V to the mole fraction y_i and to the total pressure P .

$$\text{Thus} \quad f_i^V = \phi_i y_i P \quad [1]$$

At lower pressures, around and below atmospheric, the fugacity coefficient is essentially unity (except in systems which exhibit strong chemical interactions in the gas phase), but at higher pressures it deviates widely from unity. The fugacity coefficients for gas mixtures can be calculated from an equation of state (such as the virial equation or the well established Redlich-Kwong equation) provided appropriate mixing rules are known to determine the constants for the equation of state for the mixture from the pure-component equation of state. In the present work the gas mixture was considered to be ideal since most of the tests were carried out at or near atmospheric pressure. However, the program package EQUIL does involve a subroutine which computes the fugacity coefficient at higher pressures than atmospheric.

For a non ideal liquid mixture the activity coefficient γ_i relates the liquid phase fugacity f_i^L to the mole fraction x_i and the vapor pressure P_i . Thus

$$f_i^L = \gamma_i x_i P_i \phi_i^S \exp \left[\bar{v}_i^L (P - P_i) / RT \right] \quad [2]$$

Activity coefficients for the liquid phase can be calculated from one of a number of equations developed through empirical or semitheoretical approaches, for instance Van Laar, Margules, Wilson, NRTL and UNIQUAC equations.

The vapor pressures P_i are calculated using the Antoine equation:

$$\lg P_i = A_i - B_i / (C_i + t) \quad [3]$$

where A_i , B_i and C_i are constants pertaining to the pure component i . These constants for many substances can be found in some text books, for instance reference (1).

The condition for phase equilibrium is that

$$f_i^V = f_i^L$$

The exponential term in equation [2] seldom has a value which deviates more than 1% from unity for systems that do not contain subcritical components. Because the fugacity coefficient ϕ_i is a quantitative correction factor showing the extent of the departure of actual gases from ideal behaviour and because the activity coefficient γ_i is a similar correction factor relating the behaviour of actual liquids to that of ideal liquids an evaluation of these coefficients as a function of temperature, pressure, and composition is essential to the determination of vapor-liquid equilibrium data. Because distillation operations are in practice always conducted at nearly constant pressure conditions, only the isobaric

data are useful for direct application in design calculations. Thus, the relationship between these coefficients, temperature, and composition at constant pressure is of particular interest. Furthermore, most distillation towers are operated at moderate pressures where the behaviour of the vapor phase is ideal and the fugacity coefficient ϕ_i is approximately unity (except in systems which exhibit strong chemical interactions). Because of this more effort has been extended to the study of solution nonideality through activity coefficient correlation with composition at constant pressure.

It could be concluded, therefore, that for many practical purposes the equilibrium criterion

$$y_i P = \gamma_i x_i P_i \quad [4]$$

is adequate for describing most vapor-liquid equilibrium in systems up to 100 kPa pressure. Throughout this work, equation [4] is used as the basis for the equilibrium calculations.

The program package EQUIL uses the Van Laar, Margules, and Wilson equations for the activity coefficients of binary liquid mixtures. These are written below as equations [5], [6] and [7] respectively.

$$\left. \begin{aligned} \lg \gamma_1 &= A_{12} \left(\frac{A_{21} x_2}{A_{12} x_1 + A_{21} x_2} \right)^2 \\ \lg \gamma_2 &= A_{21} \left(\frac{A_{12} x_1}{A_{12} x_1 + A_{21} x_2} \right)^2 \end{aligned} \right\} \quad [5]$$

$$\left. \begin{aligned} \lg \gamma_1 &= [B_{12} + 2(B_{21} - B_{12})x_1]x_2^2 \\ \lg \gamma_2 &= [B_{21} + 2(B_{12} - B_{21})x_2]x_1^2 \end{aligned} \right\} \quad [6]$$

$$\left. \begin{aligned} \ln \gamma_1 &= -\ln(x_1 + x_2 \Lambda_{12}) + x_2 \xi \\ \ln \gamma_2 &= -\ln(x_2 + x_1 \Lambda_{21}) - x_1 \xi \end{aligned} \right\} \quad [7]$$

$$\text{where} \quad \xi = \frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}}$$

$$\text{and} \quad \left. \begin{aligned} \Lambda_{ij} &= \frac{v_j^L}{v_i^L} \exp -[(\lambda_{ij} - \lambda_{ji})/RT] \\ \Lambda_{ji} &= \frac{v_i^L}{v_j^L} \exp -[(\lambda_{ji} - \lambda_{ij})/RT] \end{aligned} \right\} \quad [8]$$

It has been shown by many authors (2), (3) that the Wilson equation is in many respects better and more directly applicable than any other two-parameter equation. Moreover the Wilson equation has two important features which make it particularly useful for engineering applications. First, it allows the use of parameters obtained from data at one temperature to predict activity coefficients at some other temperature not too far away. This is an important advantage in the design of nearly-isobaric distillation towers where the temperature varies from plate to plate. Further, one may extend the equilibrium data for a given system to conditions of composition and temperature at which experimental information is not available. Second, Wilson's general equation for a multicomponent solution

$$\ln \gamma_k = 1 - \ln \left[\sum_{j=1}^n x_j \Lambda_{kj} \right] - \sum_{i=1}^n \frac{x_i \Lambda_{ik}}{\sum_{j=1}^n (x_j \Lambda_{ij})} \quad [9]$$

requires only parameters which can be obtained from binary mixture data. This feature provides an important economic advantage since the amount of experimental work required to characterize a multicomponent solution is thereby very much reduced. However, Wilson's equation also contains the undesirable feature of its inapplicability to liquid mixtures with only partial miscibility. In an effort to overcome this disadvantage, the modified Wilson equation (4) predicts immiscibility with only one additional parameter.

The constants in the foregoing equations can be evaluated by least squares minimization of a suitable objective function if experimental equilibrium data are available.

For binary systems only one data point would be required, theoretically, for simultaneous solution of pairs of equations. This requires an accurately determined point, such as that represented by an azeotrope composition and temperature, and a perfect model. Other points may be used if they are accurately evaluated and those determined in the middle range of concentration are usually more reliable. In general, however, it is desirable to have a series of data points, over the entire range of composition in order to get more reliable results.

In the absence of experimental data for a given system, a recently developed group-contribution method, the UNIFAC model (5), for predicting activity coefficients in nonelectrolyte liquid mixtures can be used. The basic concept in this model is that a liquid mixture can be looked upon as a solution of a relatively small number of functional groups ($-\text{CH}_3$, $-\text{CHO}$, $-\text{CHOH}$, $-\text{CHCl}_2$, etc.).

The activity coefficients of the compounds constituting a binary or multicomponent mixture for which no experimental data exist can be calculated provided parameters representing group interactions, sizes, and surface areas of the relevant groups are available from experimental information on chemically related systems. Size- and area-parameters are available from pure component molecular structure data. Group interaction

parameters for a large number of different groups including various hydrocarbon-, ketone-, aldehyde-, ester-, amine-, and chloride- groups and water are available from phase equilibrium data.

The activity coefficients are in the UNIFAC model given in terms of a combinatorial part, essentially due to differences in molecular sizes and shapes, and a residual part, essentially due to molecular interactions:

$$\ln \gamma_i = \ln \gamma_i^{\text{C}} + \ln \gamma_i^{\text{R}} \quad i = 1, 2, 3, \dots, n \quad [10]$$

combin. residual

where

$$\ln \gamma_i^{\text{C}} = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + \zeta_i - \frac{\Phi_i}{x_i} \sum_j \frac{\zeta_j}{j} \quad [11]$$

and

$$\ln \gamma_i^{\text{R}} = \sum_k \nu_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad [12]$$

all groups

$$\zeta_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad ; \quad z = 10$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad ; \quad \Phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

In these equations, x_i is the mole fraction of component i , and θ_i and Φ_i are the area and volume fractions. Pure-component parameters r_i and q_i are, respectively, measures of molecular van der Waals volumes and molecular surface areas. The parameters r_i and q_i are calculated as the sum of the group volume and area parameters, R_k and Q_k :

$$r_i = \sum_k \nu_k^{(i)} R_k \quad \text{and} \quad q_i = \sum_k \nu_k^{(i)} Q_k \quad [13]$$

where $\nu_k^{(i)}$, always an integer, is the number of groups of type k in molecule i . Group parameters R_k and Q_k are obtained from the van der Waals group volumes and surface areas (6).

In equation [12], Γ_k is the group residual activity coefficient, and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i . The term $\ln \Gamma_k^{(i)}$ is necessary to attain the normalization that activity coefficient γ_i becomes unity as $x_i \rightarrow 1$.

$$\ln \gamma_i = \ln \left[1 - \ln \frac{\sum_j \nu_j^{(i)} \gamma_j}{\sum_j \nu_j^{(i)} \gamma_j} - \frac{\sum_j \nu_j^{(i)} \gamma_j}{\sum_j \nu_j^{(i)} \gamma_j} \right] \quad [14]$$

Equation [14] also holds for $\Gamma_k^{(i)}$.

$$\Theta_m = \frac{Q_m \gamma_m}{\sum_n Q_n \gamma_n} ; \quad X_m = \frac{\sum_i \bar{v}_m^{(i)} x_i}{\sum_k \sum_i \bar{v}_k^{(i)} x_i} ; \quad \psi_{nm} = \exp(-\epsilon_{nm}/\bar{r})$$

Θ_m is the area fraction and X_m is the mole fraction for group m in the mixture. a_{nm} is the group-interaction parameter and is a measure of the difference in energies of interaction between a group n and a group m and between two groups m .

There are two group-interaction parameters per binary mixture of groups: a_{nm} and a_{mn} . These parameters are different and must be evaluated from experimental phase-equilibrium data. Parameters for 25 different functional groups in the temperature region 275-400 K have been recently published (5). The number of different functional groups included in the UNIFAC model has now reached 50, and the corresponding parameters will be published soon (7).

The program package EQUIL

The program package EQUIL, shown schematically in *fig. 1*, has two main objectives. The first objective is to compute activity coefficients to be used in DESTLA, a computer program for calculation of multicomponent distillation (8). The second objective is to plot complete equilibrium curves for binary systems using a minimum of experimental information. The package can handle the following three cases:

1. If experimental data for the system are available, ACTIVA will then compute the activity coefficients by least squares minimization of a suitable objective function.
2. Where no experimental data are available, the UNIFAC model will compute the activity coefficients of the system, provided all the functional groups involved are included in the model.
3. In cases other than those mentioned above, the ideal system concept is applied.

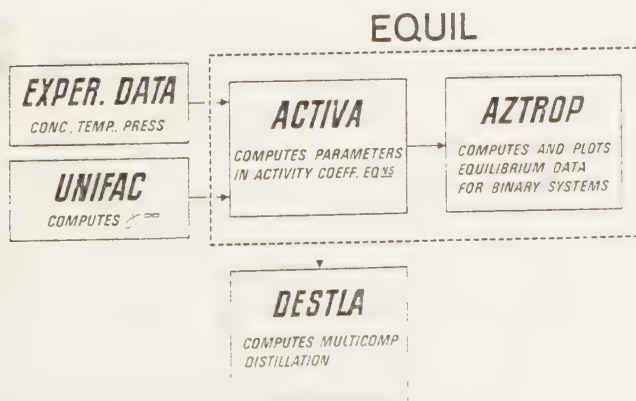


Fig. 1. Schematic flow sheet showing the different programs.

The program package EQUIL is written in FORTRAN IV and has been developed on the UNIVAC 1108 computer at the Lund Data Center. Diagrams have been plotted on the "Calcomp model 563" plotter. EQUIL comprises about 2300 punch cards and is divided into 15 subprograms including both minimization and plotting routines. It requires about 21 400 words of core memory.

The computer program ACTIVA

The computer program ACTIVA (9) computes the parameters A_{12} and A_{21} of the Van Laar equation [5], B_{12} and B_{21} of the Margules equation [6], λ_{12} and λ_{21} or $(\lambda_{12}-\lambda_{11})$ and $(\lambda_{21}-\lambda_{22})$ of the Wilson equation [7] and [8].

A flow sheet for the program ACTIVA is shown in *fig. 2*. When experimental data are available, the parameters mentioned above are computed by least square fitting to either the pressure, the vapor phase compositions, the activity coefficients, or to a combination of the pressure and the vapor phase composition. This fitting is done by minimizing one of the objective functions available in the program, equations [15]—[18] below, using an effective minimization routine (10).

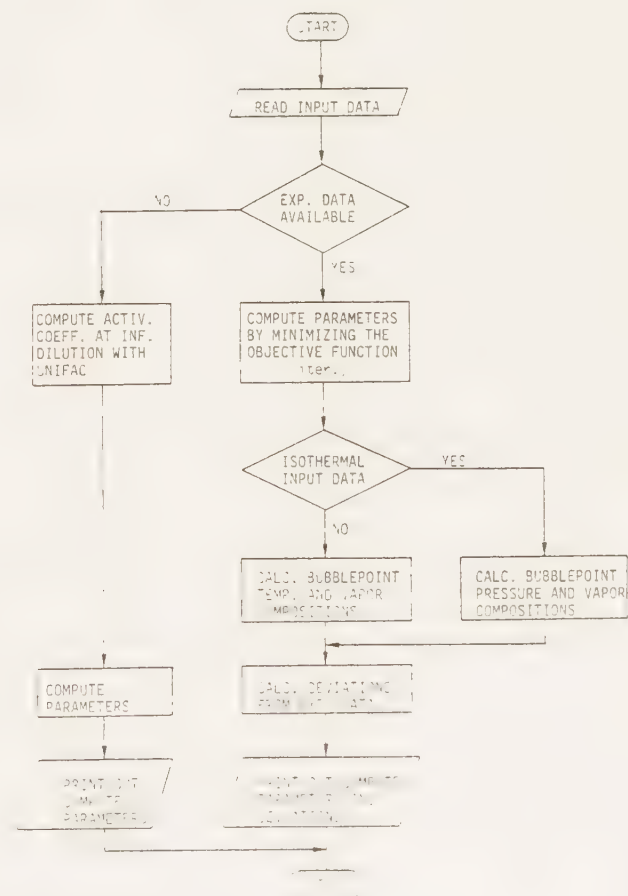


Fig. 2. Flow sheet of ACTIVA.

$$Q_0 = \sum_{i=1}^N \left(\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right)_i^2 \quad [15]$$

$$Q_1 = \sum_{i=1}^N \left(\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right)_i^2 + \sum_{i=1}^N (y_{\text{exp}} - y_{\text{calc}})_i^2 \quad [16]$$

$$Q_2 = \frac{\sum_{i=1}^N (\gamma_{1,\text{exp}} - \gamma_{1,\text{calc}})_i^2}{\sum_{i=1}^N (\gamma_{1,\text{exp}} - 1)_i^2} + \frac{\sum_{i=1}^N (\gamma_{2,\text{exp}} - \gamma_{2,\text{calc}})_i^2}{\sum_{i=1}^N (\gamma_{2,\text{exp}} - 1)_i^2} \quad [17]$$

$$Q_3 = \sum_{i=1}^N (y_{\text{exp}} - y_{\text{calc}})_i^2 \quad [18]$$

The objective functions, equations [15]–[17], have earlier been reported by Prausnitz et al. (11), Renon and Prausnitz (12), and Holmes and Van Winkle (2) respectively. The computed parameters are then used to calculate the vapor phase compositions and bubble point temperatures or pressures, depending on whether the experimental data are isobaric or isothermal. The deviations from experimental data are calculated and the program then prints out the computed parameters and the deviations. The computation of the parameters by minimizing the objective function and the calculation of bubble point temperature for isobaric data are iterative procedures.

If no experimental data are available for the binary system, the UNIFAC model can be used to predict the activity coefficients. In this case we have chosen to calculate the activity coefficients at infinite dilution (γ_i^∞). The parameters of the Van Laar, Margules, and Wilson equations are then obtained by inserting the computed values of γ_i^∞ and $x_i=0$ in equations [5]–[7] respectively. This results in the following equations:

$$\left. \begin{aligned} A_{12} &= \lg \gamma_1^\infty \\ A_{21} &= \lg \gamma_2^\infty \end{aligned} \right\} \quad [19]$$

$$\left. \begin{aligned} B_{12} &= \lg \gamma_1^\infty \\ B_{21} &= \lg \gamma_2^\infty \end{aligned} \right\} \quad [20]$$

$$\left. \begin{aligned} \ln \gamma_1^\infty &= 1 - \ln A_{12} - A_{11} \\ \ln \gamma_2^\infty &= 1 - \ln A_{21} - A_{22} \end{aligned} \right\} \quad [21]$$

It should be noted that in the case of Wilson's parameters an iterative trial and error procedure is needed. The parameters are printed out by ACTIVA. If the binary system under consideration should contain functional groups that are not yet included in UNIFAC, the only remaining alternative is to treat the system as being ideal.

The parameters of the Wilson, Van Laar, and Margules equations have been computed in this work for

several binary systems. The experimental vapor-liquid equilibrium data were taken from Hála (13). The four different objective functions available in the program, i.e. equations [15]–[18] were compared in order to find the function that gives the best parameters for predicting binary vapor-liquid equilibrium data. From those tests we recommend equation [15]. This equation gives the best correlation with experimental temperature (or pressure). It also gives a measure of the thermodynamic consistency of the experimental data by comparison of calculated and experimental vapor phase compositions, since the vapor phase compositions are not included in that equation. When using equation [18], the best correlation with vapor phase compositions is achieved on the expense of the temperature (or pressure) correlation. Where a good correlation to both vapor composition and temperature (or pressure) is desired, equation [16] or [17] should be used. In this latter case, it is rather difficult to compare the goodness of each equation separately and therefore the system under consideration should be individually tested and the best result chosen. If the binary parameters are to be used for multicomponent calculations, it is better to use equation [15].

The computer program AZTROP

The computer program AZTROP (14), the flow sheet of which is shown in *fig. 3*, calculates and plots both isobaric and isothermal equilibrium curves for binary systems. The input data required consist of Antoine's constants for the pure components according to equation [3], the two parameters for calculating the activity coefficients according to one of equations [5]–[7], the pressure or temperature for which the equilibrium data will be computed, and a specification of the information desired to be plotted. The next step is to examine whether the binary system under consideration has an azeotrope. If an azeotrope does exist, the program will compute the azeotrope. AZTROP will then compute either the isobaric or the isothermal equilibrium relationship. Different computed information, such as temperature or pressure, liquid and vapor compositions, activity coefficients, and relative volatility are printed out in a tabulated form. The program will also plot, if requested, the P - x - y , the T - x - y , the y - x , the γ_1 - x , and the α - x diagrams. AZTROP has sufficient flexibility to allow the user to choose combinations of these diagrams. They are plotted within an A4-format, together with an enlarged version (400 × 400 mm) of the equilibrium diagram for design purposes. On plotting these diagrams, except for the y - x diagram, the program will automatically scale the y - x axis to a suitable dimension for the maximum and minimum values computed for each function.

The CPU-time consumption for the program package EQUIL to compute a complete vapor-liquid equilibrium information for one binary system using 15 experimental data points is about 2 seconds. If all the diagrams mentioned above are to be plotted, EQUIL will consume about 8 seconds in CPU-time and 11 plotting minutes.

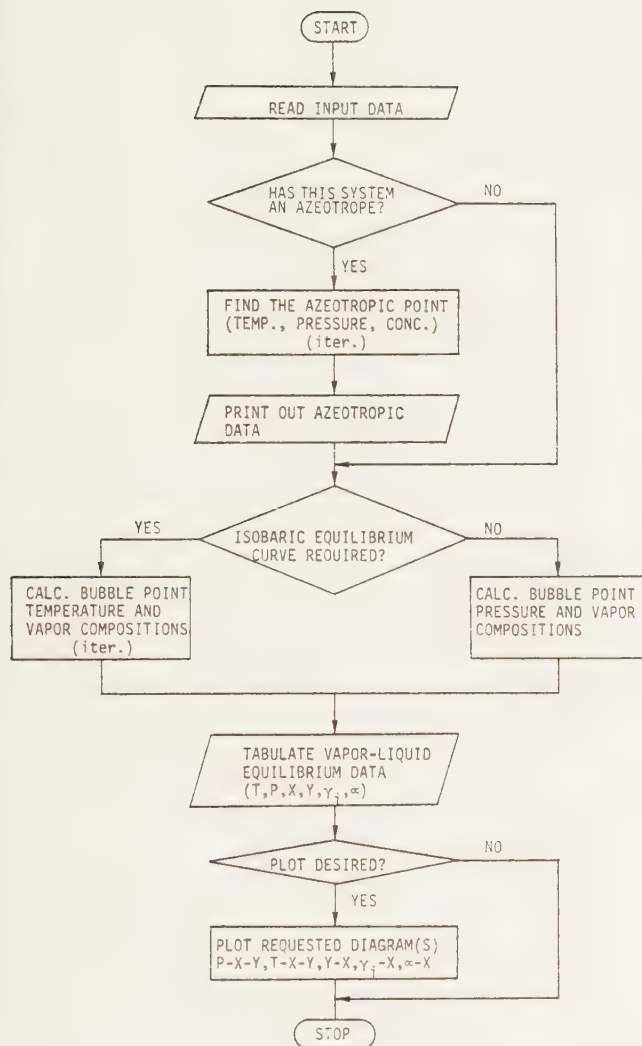


Fig. 3. Flow sheet of AZTROP.

All the iterative computations involved in both ACTIVA and AZTROP are greatly accelerated by ADJUST, an adaptive convergence algorithm for general trial and error computations (15).

Results

The program package EQUIL can be demonstrated with 4 numerical examples. The first example deals with a standard binary nonazeotropic system for which experimental equilibrium data are well-known. The second example deals with an azeotropic system and shows the effect of pressure on the azeotropic properties. The third example compares the UNIFAC model, Wilson's equation, and the ideal-solution concept. The last example demonstrates how the computed activity coefficients for binary systems can be used in computations dealing with multicomponent distillation.

Antoine's constants for the components in all systems involved in the following examples were taken from reference (1).

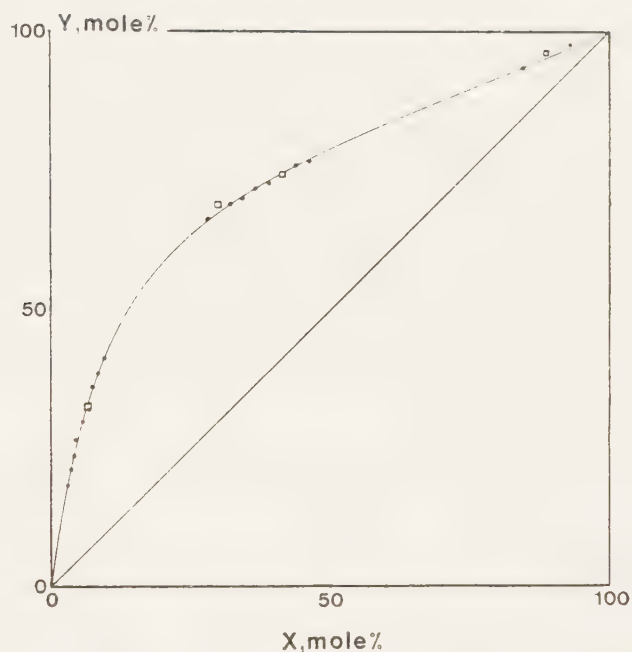


Fig. 4. Equilibrium curve for methyl alc.-water at 101.3 kPa. ● = exp. data, □ = exp. data used in curve fitting; full line: computed curve using 4 exp. data points.

Numerical example no. 1

Isobaric experimental equilibrium data for the well-known methyl alcohol-water system at 101.3 kPa are available in reference (13). Four of the 21 published data points were arbitrarily chosen as a basis for prediction of the complete equilibrium curve. ACTIVA computed Wilson's parameters as $\Lambda_{12} = 0.4374$ and $\Lambda_{21} = 1.0053$ using the first objective function, equation [15]. Wilson parameters together with Antoine constants and the total pressure value of 101.3 kPa were then used in AZTROP to compute and plot the equilibrium information for this system. The equilibrium curve obtained is shown as the full line in fig. 4. The experimental data points are also marked. The mean deviations between the computed curve and all experimental points are 0.004 mole fraction in vapor phase composition and 0.3°C in temperature. The mean deviations were calculated according to the equation:

$$\sigma = \frac{\sum_{j=1}^N |\sigma_{\text{exp}, j} - \sigma_{\text{calc}, j}|}{N} \quad [22]$$

where σ is either vapor phase composition y , temperature T , or pressure P and N is the number of experimental data points.

The computed Wilson parameters were further used to extrapolate the equilibrium curve to a temperature of 50°C for which there is experimental data available (13). A comparison between the computed equilibrium curve

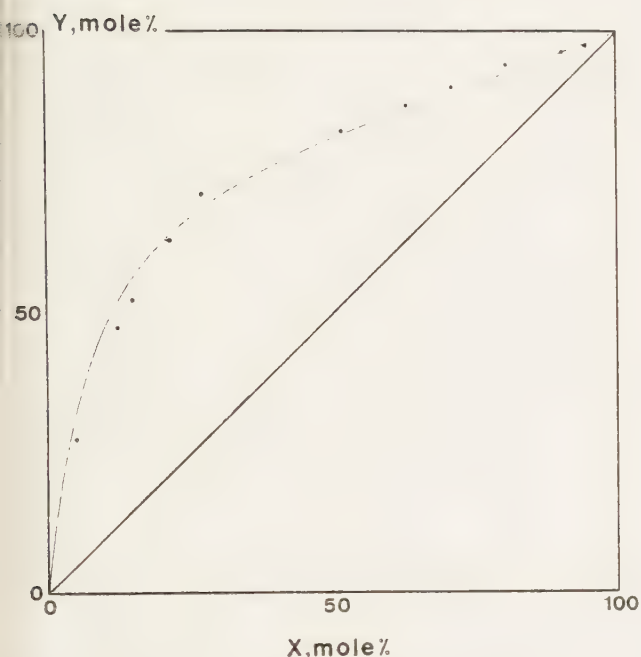


Fig. 5. Equilibrium curve for methyl alc.-water at 50°C. ● = exp. data; full line: computed curve using data at 101.3 kPa.

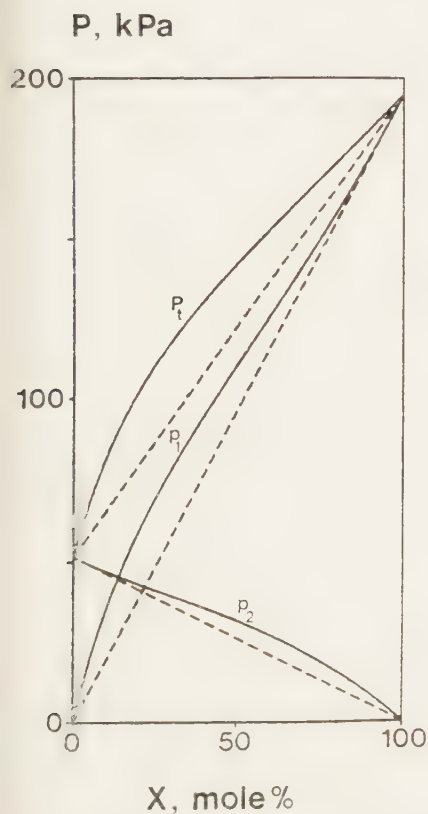


Fig. 6. P - x diagram, numerical example no. 1. Dashed lines: using Raoult's law (ideal); full lines: using Wilson's equation.

and the experimental data is shown in *fig. 5*. The mean deviations in this case are 0.019 mole fraction in vapor phase composition and 1.6 kPa in pressure.

Fig. 6—fig. 9 illustrate the equilibrium information which can be plotted by AZTROP. The pressure-liquid composition diagram, *fig. 6*, is computed for a temperature which is an average of the boiling points of the pure components at the prevailing pressure. The linear relationship between partial pressure and liquid composition is calculated by Raoult's law and plotted as dashed lines for comparison. As can be seen from the diagrams for pressure-liquid composition, *fig. 6*, the activity coefficient-liquid composition, *fig. 8*, and the

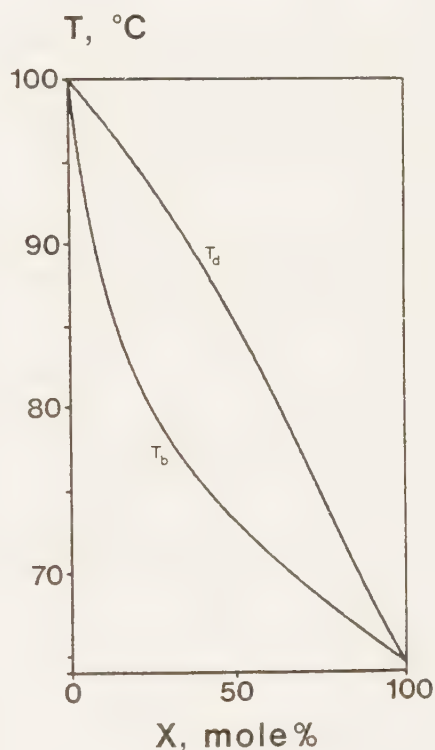


Fig. 7. T - x - y diagram, numerical example no. 1.

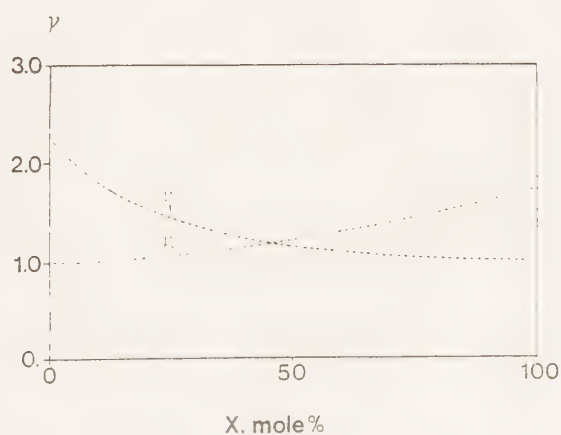


Fig. 8. γ_1 - x diagram, numerical example no. 1.

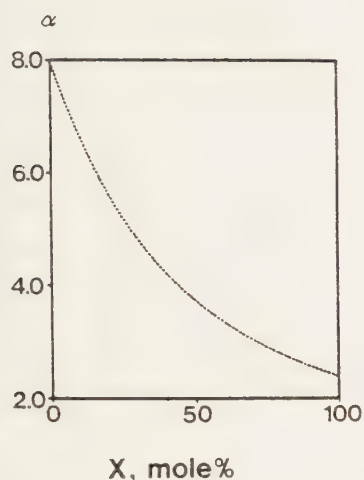


Fig. 9. α - x diagram, numerical example no. 1.

relative volatility-liquid composition, fig. 9, the methyl alcohol-water system should not be treated according to the ideal-solution concept.

It can be seen from this example that one can compute an equilibrium curve with an acceptable engineering accuracy using only few experimental data points. These points should however be of good thermodynamic consistency and should cover most of the composition range. For a reliable equilibrium curve, one should of course use all the experimental data points available. It is thus possible to compute equilibrium information at some pressure, or also at some temperature for which experimental data are missing. However, one should be careful not to extrapolate too far from experimental temperatures or pressures since the activity coefficients are also functions of temperature.

Numerical example no. 2

In some cases, only the azeotropic properties of a binary azeotropic system are known. Since theoretically only one data point is required to solve for the parameters in the activity coefficient equations, it is possible to compute the equilibrium curve using only the azeotropic point. To demonstrate this possibility, we have chosen the ethyl alcohol—water system as an example. Azeotropic data for this system at 101.3 kPa give 0.895 mole fraction ethyl alcohol and 78.15°C (16). Using this accurately determined data point, ACTIVA computed Wilson's parameters $A_{12}=0.1382$ and $A_{21}=0.9078$. AZTROP plotted the equilibrium curve shown in fig. 10 where experimental data points, published in (13), are marked for comparison. The mean deviations between the computed curve and the experimental data points are 0.020 mole fraction in vapor phase composition and 0.7°C in temperature.

It is sometimes useful to know the effect of pressure on the composition of an azeotrope since it may be possible to make the azeotrope disappear by operating at a higher or lower pressure than atmospheric. In some cases there may be an azeotrope at some other pressure

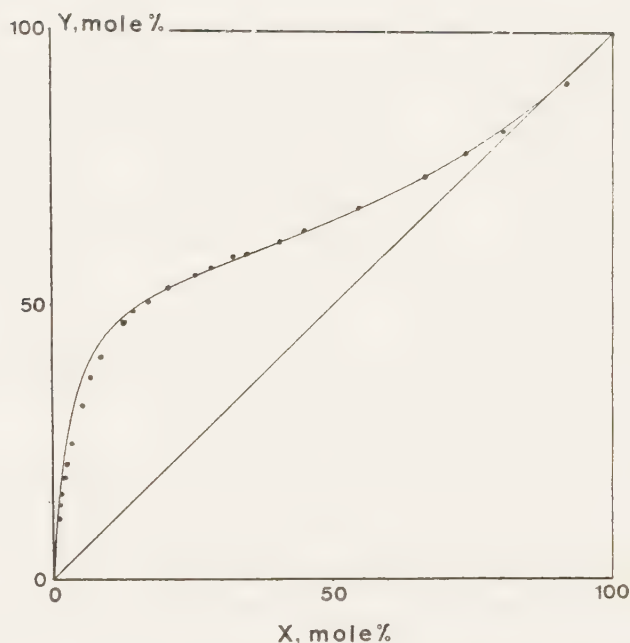


Fig. 10. Equilibrium curve for ethyl alc.-water at 101.3 kPa. ● = exp. data; full line: computed curve using the azeotropic point only.

and none at atmospheric. For this purpose we have tested the effect of pressure on the azeotropic properties of this system. The results are shown in table 1 together with a comparison between the calculated values, computed by AZTROP, and the experimental values published in reference (17).

If the azeotropic point is near the end points of the composition range the computed equilibrium curve may be less reliable. However, in all the binary azeotropic systems tested in this work this equilibrium curve was better than that obtained using the ideal-solution concept. Table 1 shows the necessity for care in extrapolating data to temperature or pressure values far from those for which the activity coefficients are calculated.

Table 1. Effect of pressure on the azeotrope in the system ethyl alc.-water

Pressure kPa	Azeotropic point			
	Temperature, °C		Composition, mole %	
	Calc.	Exp.	Calc.	Exp.
17.3	39.3	39.2	93.3	96.7
26.4	47.7	47.6	92.4	93.4
54.0	63.1	63.0	90.8	90.9
101.3	78.1	78.1	89.3	89.5
143.3	87.1	87.1	88.4	88.9
193.5	95.3	95.3	87.7	88.7
344.6	112.4	112.6	86.2	88.2

Table 2. Comparison between experimental and calculated activity coefficients

x_1	x_2	x_3	Experimental activity coefficients				Calculated activity coefficients			
			γ_1	γ_2	γ_3	γ_4	γ_1	γ_2	γ_3	γ_4
0.733	0.052	0.157	1.12	1.20	4.27	1.70	1.09	1.13	4.46	1.42
0.743	0.105	0.107	1.06	1.15	5.90	1.55	1.05	1.08	5.85	1.40
0.732	0.111	0.035	1.01	1.06	12.40	1.42	1.01	1.03	9.20	1.36
0.742	0.057	0.090	1.06	1.10	6.51	1.48	1.04	1.07	6.26	1.36
0.139	0.166	0.514	2.11	1.97	1.50	1.79	2.08	1.97	1.47	1.73
0.156	0.510	0.154	1.20	1.16	4.20	1.34	1.15	1.12	4.24	1.28
0.330	0.076	0.515	1.92	1.91	1.49	1.84	1.90	1.86	1.53	1.82
0.354	0.208	0.365	1.43	1.43	2.06	1.57	1.45	1.44	2.12	1.56
0.359	0.360	0.165	1.18	1.14	4.05	1.40	1.13	1.12	4.15	1.34
0.371	0.502	0.034	1.20	1.05	12.06	1.35	1.02	1.02	9.68	1.34

Numerical example no. 3

To demonstrate the group-contribution method, UNIFAC, we have chosen a prediction of the vapor-liquid equilibrium for a four-component system. The UNIFAC-model is also compared in this example with both the Wilson equation, which requires experimental data for the six binaries involved in this system, and the ideal-solution concept (Raoult's law).

The quaternary system *n*-hexane-methylcyclopentane-ethyl alcohol-benzene at 101.3 kPa was chosen for study. This system is an especially severe test of UNIFAC since mixtures of isomers such as methylcyclopentane were not included in the data base. The components will be referred to as components 1—4 respectively. Experimental equilibrium data for the six binaries and for the quaternary system are given in references (13), (18), and (19). The UNIFAC-model was used to predict the activity coefficients for the chosen system. The computed results are shown in table 2 where the values obtained are compared with the activity coefficients calculated using experimental data. As can be seen, the UNIFAC-model agrees well with the experimental results.

ACTIVA computed the parameters of the Wilson equation for the six binaries. The equilibrium data for the quaternary system were then computed using activity coefficients, from UNIFAC and from Wilson's equation, and using the ideal-solution concept. Table 3 gives the mean deviations between experimental and calculated vapor phase compositions, for these three methods. The mean deviation for each component was calculated according to equation [22].

Table 3. Mean deviations (mole fraction) between experimental and calculated vapor phase compositions

Component	UNIFAC model	Raoult's law	Wilson's equation
1	0.011	0.079	0.006
2	0.012	0.056	0.003
3	0.026	0.225	0.008
4	0.010	0.040	0.009

It can be seen from table 3 that the UNIFAC-model predicts the vapor phase compositions much better than the ideal-solution concept using Raoult's law, especially for the third component where the activity coefficients deviate greatly from unity. However, Wilson's equation should be used for systems where experimental data are available. If experimental data are not available for one or more of the binaries involved in a given multicomponent system, the UNIFAC-model provides an accurate tool for predicting the missing activity coefficients. One possible way to achieve this is to compute the activity coefficients at infinite dilution and then apply equation [21] to obtain the Wilson parameters.

Numerical example no. 4

The purpose of this example is to illustrate the main goal of vapor-liquid computations; namely to use this information for distillation tower design calculations. The activity coefficients for binary systems computed by ACTIVA are used mainly to calculate multicomponent distillation by means of the computer program DESTLA. This is shown in fig. 1.

DESTLA is based on the principles of modular composition of general distillation plants and uses so-called unit cells together with a description of the plant flow sheet as a connection matrix. The unit cell is a module which enables the user to assemble flow sheets of distillation plants of arbitrary complexity. The module used here comprises a tower plate, a flasher, a reboiler, a total condenser, a partial condenser, a heat exchanger, a liquid mixing vessel, a vapor mixing vessel, and a liquid separation vessel.

As a typical run for DESTLA, we have chosen the separation of methyl alcohol and acetone by extractive distillation using water as solvent, according to the flow sheet shown in fig. 11. Methyl alcohol and acetone form a minimum boiling point azeotrope at 23 mole per cent methyl alcohol (at atmospheric pressure) but the addition of water increases the relative volatility of acetone until the azeotrope vanishes. The Wilson parameters used for calculating the activity coefficients for this ternary system were computed by ACTIVA from binary vapor-liquid equilibrium data (13). Wilson's equation

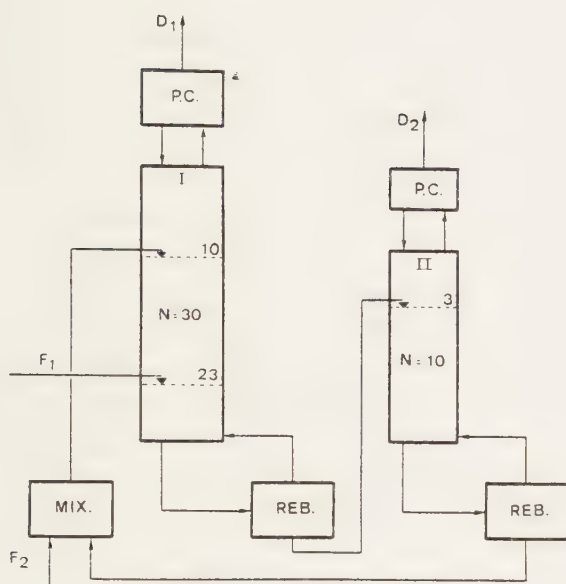


Fig. 11. Flow sheet for extractive distillation in the system acetone (1)—methyl alcohol (2)—water (3).

REB. = Reboiler
P. C. = Partial Condenser
MIX. = Liquid mixing vessel
N = number of plates

for multicomponent systems, equation [9], is used in DESTLA to compute the vapor-liquid equilibria. The following Wilson's parameters were computed for the system under consideration:

$$\begin{aligned} A_{12} &= 1.2602 & A_{21} &= 0.3651 \\ A_{13} &= 0.2461 & A_{31} &= 0.4291 \\ A_{23} &= 0.4269 & A_{32} &= 1.0164 \end{aligned}$$

In the flow sheet of fig. 11, the saturated binary liquid, F_1 , is fed to the first tower on plate 23 while the solvent, in this case water, is fed on plate 10 in the same tower. The solvent stream consists of the recovery from the second tower and a make-up, F_2 , compensating for the small losses in the product streams, D_1 and D_2 . The bottom stream leaving the first tower is fed to plate 3 in the second tower for solvent recovery. Both towers are assumed to operate at atmospheric pressure. A summary of the results computed by DESTLA is shown in table 4.

Table 4. Results computed by DESTLA for numerical example no. 4

Stream	Flow rate kmole/h	Temperature °C	Composition, mole fraction		
			Acetone	Methyl alc.	Water
F_1	100.0	55.4	0.750	0.250	0.0
F_2	6.0	100.0	0.0	0.0	1.0
D_1	77.9	56.0	0.917	0.054	0.029
D_2	28.1	68.2	0.100	0.773	0.127

For this type of distillation calculation involving non-ideal systems, it is necessary to be able to compute the activity coefficients using a suitable model such as the Wilson equation. Applying the ideal-solution concept in this case would definitely lead to erroneous results.

Conclusions

The program package EQUIL is a suitable tool for the design engineer to compute and plot vapor-liquid equilibria, using only a few experimental data points, with an acceptable engineering accuracy. It allows the calculation of equilibrium information for a given system at some temperature or pressure value different from that at which experimental data are available. It is for instance often useful to know the effect of pressure on the composition of an azeotrope in order to see if it is possible to make the azeotrope disappear by changing the total pressure of the system. In such cases, an extrapolation procedure is easily carried out by EQUIL. However, care should be taken not to extrapolate too far from experimental temperatures or pressures.

When no experimental data are available, the UNIFAC model may be used to predict vapor-liquid equilibria. A given multicomponent system contains a number of constituent binary systems. In many cases, experimental activity coefficients may be available for some, but not all, of these binaries. UNIFAC may be used here to predict the activity coefficients for each of the components in the unknown binaries. These predicted activity coefficients can then be used to compute Wilson parameters which in turn allow the calculation of vapor-liquid equilibria for multicomponent systems.

Acknowledgements

The authors wish to express their sincere gratitude to Dr Aage Fredenslund at Inst. for Kemiteknik, The Technical University of Denmark for his valuable assistance and constructive discussions in the course of this work.

List of symbols

a_{nm}	UNIFAC binary group-interaction parameter
A_1, B_1, C_1	constants in Antoine's equation [3]
A_{12}, A_{21}	parameters in Van Laar's equation [5]
B_{12}, B_{21}	parameters in Margules equation [6]
f_i^V	the fugacity of component i in the vapor phase, kPa
f_i^L	the fugacity of component i in the liquid phase, kPa
n	number of components
N	number of experimental data points

p_i	partial pressure, kPa
P	total pressure of the system, kPa
P_i	vapor pressure of pure component, kPa
q_i	pure-component area parameter, defined in equation [13]
Q	objective function
Q_k	group area parameter
r_i	pure-component volume parameter, defined in equation [13]
R	gas law constant, cal/g mol/K
R_k	group volume parameter
t	temperature, °C
T	temperature, K
$v, \bar{v}$	molar volume and partial molar volume, cc/g mol
x_i	liquid phase composition, mole fraction
X_m	liquid phase group fraction, defined after equation [14]
y_i	vapor phase composition, mole fraction
z	lattice coordination number, a constant here set equal to ten

Greek letters

α	relative volatility
γ_i	activity coefficient correlating for nonideality in liquid phase
Γ_k	residual activity coefficient of group k, defined by equation [14]
$\Gamma_k^{(i)}$	residual activity coefficient of group k in pure component i
θ_i	area fraction of component i, defined after equation [12]
Θ_k	area fraction of group k, defined after equation [14]
λ_{ij}	parameters in Wilson's equation [8], cal/g mol
$\lambda_{12}, \lambda_{21}$	parameters in Wilson's equation [7]
$\nu_k^{(i)}$	number of groups of type k in a molecule of component i
ϕ_i	fugacity coefficient correlating for nonideality in gas phase
Φ_i	segment or volume fraction of component i, defined after equation [12]

Subscripts

i, j, k	component i, j and k
k, m, n	group k, m and n
exp	experimental values
calc	calculated values

Superscripts

C	combinatorial
L	liquid phase
R	residual
s	pure saturated state
∞	infinite dilution

Literature

1. Boublik, T., Fried, V. and Hála, E.: The vapour pressures of pure substances. Elsevier, Amsterdam (1973).
2. Holmes, M. J. and Van Winkle, M.: Ind. Eng. Chem. 62 (1970): 1, p. 21.
3. Nagata, I.: J. Chem. Eng. Jap. 6 (1973): 1, p. 18.
4. Scatchard, G. and Wilson, G. M.: J. Amer. Chem. Soc., 86 (1964), p. 133.
5. Fredenslund, A., Jones, R. L. and Prausnitz, J. M.: A.I.Ch.E. Journal 21 (1975), p. 1086.
6. Bondi, A.: Physical properties of molecular crystals, liquids and glasses. Wiley, New York (1968).
7. Fredenslund, A., Gmehling, J., Michelsen, M. L., Rasmussen, P., and Prausnitz, J. M. (To be published 1977.)
8. Zacchi, G. and Jernqvist, A.: "DESTLA—a computer program for calculation of general multicomponent distillation systems", Dep. of Chem. Eng., Lund Institute of Technology. (To be published 1977.)
9. Zacchi, G. and Jernqvist, A.: "ACTIVA—a program for computation of activity coefficients for vapor-liquid equilibria from experimental data", Dep. of Chem. Eng., Lund Institute of Technology (1975) Report No 75-F-3.
10. Jernqvist, A. and Zacchi, G.: "MINIMA—a computer program for curve fitting procedures", Dep. of Chem. Eng., Lund Institute of Technology (1975). Report No 75-F-2.
11. Prausnitz, J. M., Eckert, C. A., Orye, R. V. and O'Connell, J. P.: Computer calculations for multicomponent vapor-liquid equilibria. Prentice Hall, Englewood Cliffs N. J. (1967).
12. Renon, H. and Prausnitz, J. M.: A.I.Ch.E. Journal 14 (1968): 1, p. 135.
13. Hála, E., Wichterle, I., Polák, J. and Boublik, T.: Vapor-liquid equilibrium data at normal pressures, Pergamon Press, Oxford (1968).
14. Aly, G. and Jernqvist, A.: "AZTROP—a computer program for calculation and plotting of vapor-liquid equilibrium data for binary distillation systems", Dep. of Chem. Eng., Lund Institute of Technology (1974). Report No 74-F-5.
15. Jernqvist, A.: "ADJUST—an adaptive convergence algorithm for general trial and error computations", Dep. of Chem. Eng., Lund Institute of Technology (1975). Report No 75-F-1.
16. Advances in Chemistry Series 116: Azeotropic Data-III. American Chem. Soc., Washington (1973).
17. Reuther, J. A. and Lu, B. C. Y.: Can. J. Chem. Eng. 50 (1972), p. 266.
18. Ehrett, W. E. and Weber, J. H.: J. Chem. Eng. Data 4 (1959), p. 142.
19. Weber, J. T. et al.: J. Chem. Eng. Data 7 (1962), p. 344.

(Manuscript received September 27, 1976)

DESTLA - A COMPUTER PROGRAM FOR SIMULA-
TION OF THE STEADY-STATE BEHAVIOR OF
GENERAL DISTILLATION SYSTEMS

ZACCHI, G.

DEPARTMENT OF CHEMICAL ENGINEERING
LUND INSTITUTE OF TECHNOLOGY
LUND
SWEDEN

Författare

Dec 1978

Guido Zacchi

Dokumenttitel och undertitel

DESTLA - a Computer Program for Simulation of the Steady-State Behavior of General Distillation Systems.

Referat (sammandrag)

A computer program DESTLA, for simulation of the steady-state behavior of general distillation systems, has been developed. The program is based on a modular approach to flowsheeting which enables the user to assemble flowsheets of distillation plants of arbitrary complexity. Furthermore, DESTLA uses replaceable models for vapor-liquid equilibria and enthalpy data which further increases the flexibility of the program. The program was applied to solve problems involving both ideal and non-ideal mixtures as well as configurations containing interlinked columns.

Referat skrivet av

G. Zacchi

Förslag till ytterligare nyckelord

Flowsheeting, modeling, multiple towers

Klassifikationssystem och -klass(er)

Indextermer (ange källa)

Omfång

69 pages

Språk

English

Sekretessuppgifter

Dokumentet kan erhållas från

Department of Chemical Engineering,
Chemical Center, P.O.B. 740,
S-220 07 Lund 7, Sweden

Pris

Övriga bibliografiska uppgifter

ISSN

ISBN

Mottagarens uppgifter

SUMMARY

A computer program DESTLA, for simulation of the steady-state behavior of general distillation systems, has been developed. The program is based on a modular approach to flowsheeting which enables the user to assemble flowsheets of distillation plants of arbitrary complexity. Furthermore, DESTLA uses replaceable models for vapor-liquid equilibria and enthalpy data which further increases the flexibility of the program.

DESTLA can be regarded as a flowsheeting program for distillation systems although it is recognized that the list of unit operations, comprising a plate, a flasher, a reboiler, a partial condenser, a total condenser, a heat exchanger, a liquid mixing vessel, a vapor mixing vessel and a liquid separation vessel, is not so comprehensive compared to general flowsheeting programs. It should be noted however that the unit operations are provided in subroutine form and thus easily allow for the addition of further modules.

The necessary input data for an execution of DESTLA consists mainly of the flowsheet, flow rate and properties for all incoming streams, heat transfer data and component data. These data are tested and subsequently echoed in a print out in order to avoid absurd input data. As output information, DESTLA delivers all important data calculated such as flow rate, pressure, temperature, heat content and composition of all streams entering and leaving each piece of equipment in the configuration. These data are printed out in fully written out text.

For the solution of the non-linear equations modeling the various unit operation modules, a plate-to-plate method is chosen. The method has proved to be very stable for a wide range of difficult problems. Moreover, it requires a minimum of memory storage and uses a reasonably small amount of computer time although the latter could be improved in some cases using a convergence acceleration technique.

Four test examples are presented which demonstrates DESTLA's abilities well. The program was applied to solve problems involving both ideal and non-ideal mixtures as well as configurations containing interlinked columns. Furthermore, a problem involving a mixture of wide-boiling components is solved after a slight modification of the solution method.

The numerical stability and inherent flexibility combined with very simple data input procedure and self-explanatory print out of computed results make DESTLA a very useful tool for the design and process engineer. This has been proved during the last two years where DESTLA has been used for simulation and design of some industrial distillation plants in Sweden.

CONTENTS

	page
1. INTRODUCTION	1.
2. DESIGN OF THE COMPUTER PROGRAM DESTLA	9.
2.1 The unit cell	10.
2.2 Plate	12.
2.3 Flash-drum, reboiler and partial condenser	13.
2.4 Total condenser	13.
2.5 Heat exchanger	14.
2.6 Mixing vessels	14.
2.7 Separation vessel for liquids	15.
3. MODELING THE EQUIPMENT OF THE UNIT CELL	16.
3.1 Plate modeling	16.
3.2 Modeling of auxiliary equipment	19.
4. SOLUTION METHOD AND CONVERGENCE CRITERIA	21.
4.1 Solution method	21.
4.2 Convergence criteria	23.
5. PROGRAM OPERATION	25.
5.1 Input of data	25.
5.2 Input data testing and diagnostic messages	26.
5.3 Calculations	27.
5.4 Output of data	28.
6. TREATMENT OF PHASE EQUILIBRIA AND ENTHALPY	30.
6.1 Phase equilibrium models	30.
6.2 Enthalpy models	33.
7. COMPUTED EXAMPLES	36.
7.1 Example 1	36.
7.2 Example 2	37.
7.3 Example 3	38.
7.4 Example 4	39.
7.5 Conclusions	40.

ACKNOWLEDGEMENTS

LIST OF SYMBOLS

REFERENCES

APPENDICES

Appendix 1: Unit cell

Appendix 2: Typical output list from DESTLA

Appendix 3: Tables for the computed examples

Appendix 4: Figures for the computed examples

Appendix 5: Modified solution method for systems of wide-boiling
components

1. INTRODUCTION

The equations modeling a multicomponent distillation system operating at steady-state are highly non linear and interdependent. Hence, the calculations that are necessary to solve them are intrinsically iterative, complex and large in number. This necessitated a variety of simplifying assumptions on which early solution methods were based. The advent of computers in the late 1950's resulted in an increased interest in the rigorous methods, which were often based on elaborate techniques due to the inefficiency of computers at that time. The modern high-speed, large-storage computers have overcome these difficulties and made it possible to use efficient techniques for solving the equations. Most recent methods are oriented to the solution of general distillation problems, and can handle non-ideal mixtures and interlinked complex column configurations.

The first method for performing multicomponent distillation calculations appeared in 1932 and was developed by Lewis and Matheson¹. This method is essentially a design calculation where the column configuration is determined to meet desired separation specifications and reflux ratio. Since this pioneer work, many papers have appeared proposing different techniques for obtaining a rigorous solution to distillation problems. Almost all of these methods deal with the operating problem where the separation that can be obtained with a given column configuration under given conditions is to be determined. Most of the methods can be classified using one of the following categories:

- A. Plate-to-plate methods
- B. Matrix methods
- C. Relaxation methods

All rigorous models describing an equilibrium stage involve sets of simultaneous equations to express the component mass balances, into which are built a prescribed phase equilibrium model, the energy balance and the summation of liquid and vapor mole fractions. The above grouping of methods is related to the technique used for solving the set of component mass balances, which is the most important feature of the complete solution method.

The above mentioned solution methods will be briefly outlined below.

A. Plate-to-plate methods

In the literature the "plate-to-plate method" commonly refers to all methods where the component mass balances are solved for each individual stage, one stage at a time. However, it is advisable to separate these methods from the group of plate-to-plate methods where all the modeling equations are solved stage-wise. The Lewis-Matheson method mentioned earlier is an example from the latter group. In this procedure, the product compositions consistent with the specifications and the overall balances are estimated. Then plate-to-plate computations are carried out according to Sorels method² from both the top and the bottom of the column towards the feed plate. On each plate the temperature is calculated iteratively by performing either bubble point or dew point calculations. The resulting mis-match of compositions at the feed plate is then used to re-estimate the product compositions. A suitable method for this updating is presented by Bonner³. The whole procedure is then repeated until a satisfactory match of compositions is obtained.

This method has proved to be unstable under certain conditions^{4,5}. Difficulties are also to be expected for highly non-ideal systems where product compositions are unlikely to be estimated with enough accuracy.

An example from the other group of plate-to-plate methods, where only the component mass balances are solved during the stage-wise calculations, is the method of Thiele and Geddes⁶. This method avoids the estimation of product compositions but requires an estimate of the equilibrium ratios for all the plates. Once the component mass balances are solved, by plate-to-plate calculations, the product distribution (d_i/b_i for all components) is determined. This, together with an overall component mass balance, gives the product compositions. Then new equilibrium ratios are estimated and the whole procedure is repeated until convergence is reached. As no product compositions are used during the plate-to-plate calculations this method avoids the problem of instability which may rise in the Lewis-Matheson method. However, accumulation of rounding errors can give arise to numerical instabilities when multiple feeds or side-cut streams are involved.

This is due to a difference term which appears in the component mass balance whenever such an external stream is enveloped.

The Thiele-Geddes method was greatly improved by Lyster et al.⁷ who introduced the well-known " θ -method" to accelerate convergence. A factor, θ , is used for correcting the product distribution obtained in each iteration. The determination of this correcting factor requires the solution of a set of non-linear equations equal in number to the number of feeds and side-cut streams. An algorithm, including the θ -method of convergence, for handling non-ideal mixtures in complex distillation columns was presented by Billingsley⁸. This method was further extended to handle multiple distillation column configurations⁹.

According to Holland et al.¹⁰, the θ -method is recognized as one of the fastest known methods for both conventional and complex distillation columns. It has been further developed to effectively solve absorber, stripper and reboiled absorber problems¹¹. The method, called the multi- θ -method, determines the θ values by solving the set of non-linear equations with the Newton-Raphson technique.

B. Matrix methods

In 1958, Amundson and Pontinen¹² discovered that if equilibrium ratios and flow rates in a distillation column are estimated, the component mass balances can be decoupled, thus obtaining a set of linear simultaneous equations for each component. The authors presented a matrix manipulation method for solving these equations and the method was later extended to handle complex columns¹³.

By ordering these equations, they can easily be solved by various techniques for sparse matrices. Wang and Henke¹⁴ ordered the equations to form a tridiagonal matrix for each component and solved these with the "Thomas algorithm"¹⁵, which is a highly efficient method for solving sets of linear equations represented by a tridiagonal matrix. This algorithm was modified by Boston and Sullivan¹⁶, who found that the original method is subject to excessive round-off errors under certain conditions.

Sargent and Murtagh¹⁷ discovered that the method of Amundson and Pontinen failed to converge for some problems and modified the compu-

tation scheme. The modification consisted mainly of introducing an internal loop in which the equilibrium ratios were corrected until the summation equation on each plate was satisfied. Furthermore, they extended the method to deal with real plates by introducing both Murphree plate efficiency and thermal efficiency.

Beside the different techniques of solving the component mass balance matrix, the methods may differ in the procedure used for estimation of temperature and flow rates. This is very well outlined by Friday and Smith¹⁸ who described the difference between the bubble-point (BP) method and the sum-rates (SR) method. In the BP method the temperature on each plate is obtained from the summation equation, corresponding to a bubble-point or dew-point calculation, while the flow rates are obtained by solving the energy balance. This procedure is the most commonly used^{12,13,14}. In the SR method, the flow rates are obtained from the summation equation and the plate temperature from the energy balance. This method was applied to absorbers by Smith⁴, and to distillation of wide-boiling components by Friday and Smith¹⁸. The BP method seems to be suitable for systems of narrow-boiling components and numerically unstable for wide-boiling components while the opposite is true of the SR method.

To overcome the disadvantage of using either the BP or the SR method, Tomich¹⁹ extended the Amundson and Pontinen method. In this work, component mass balances were solved using the Thomas algorithm and a new set of temperatures and flow rates were obtained by solving summation equations and energy balances simultaneously. A modified Newton-Raphson procedure was applied.

A recently-developed method based on the technique of Amundson and Pontinen was presented by Hutchison and Shewchuk²⁰. The equations for each component were treated as a large set of linear equations which were solved with a technique for the repeated solution of large sparse sets of linear equations²¹. The model equations were linearized using a special treatment of equilibrium and enthalpy. The vapor-liquid equilibrium relationship was based on the assumption of locally constant relative volatilities which resulted in a much better linear approximation than the usual vapor-liquid equilibrium relationship ($y_i = K_i x_i$). New temperatures and relative volatilities were determined in each iteration by performing bubble-point calculations on each plate. Accord-

ing to the authors, the method is particular well suited to the treatment of multiple column arrangements with a modest number of components. Difficulties may be encountered for strongly non-ideal systems where the relative volatilities are sensitive to temperature and composition. In such cases, some techniques for relaxation of the volatilities are required. The main advantage of this method is the great freedom in the choice of constraints and specifications allowed.

A method, quite different from the previous matrix methods, based on the simultaneous solution of the complete set of linearized energy and mass balance equations was proposed by Goldstein and Stanfield²² and Naphtali and Sandholm²³. These two methods differ mainly in the manner of ordering the equations; the former authors grouped the equations component-wise while the latter grouped them stage-wise. Both methods use the Newton-Raphson procedure for solving non-linear equations. The simultaneous solution of all the equations makes these two methods applicable to complex distillation columns comprising systems of both narrow- and wide-boiling components. Another advantage is an enhanced convergence as the final solution is approached, due to linearization of the equations. The disadvantages of these methods are large computer storage, due to the computation of the Jacobian matrix, and evaluation of the various partial derivatives, which requires differentiation of the physical data. Furthermore, initial assumptions of all variables must not be too inaccurate, as otherwise the Newton-Raphson linearization procedure may fail to converge.

The method was improved by Ishii and Otto²⁴ by reducing the number of partial derivatives to be evaluated as well as the computer storage requirements. A similar method, suitable for multicolumn systems, was developed by Harclerode and Gentry^{25,26} using their own algorithms for solving block band matrices.

C. Relaxation methods

This is a group of methods which make use of the transient equations for the determination of steady-state solution. Such a method for distillation calculations was first proposed by Rose et al.²⁷. Their method required an initial estimate of flow rates, liquid compositions, and temperature on each plate. Equilibrium vapor compositions on each plate were evaluated. Then a new set of liquid compositions was obtained by

solving the unsteady-state component mass balances. The difference in component flow rates entering and leaving each plate was multiplied by a relaxation factor and added to the liquid compositions from the previous iteration. The liquid compositions were normalized and the whole procedure was repeated until steady-state compositions were obtained. The reciprocal value of the liquid holdup on the plate was used as a relaxation factor. The authors recommended a liquid holdup greater than at least five times the value of the feed rate to avoid numerical instabilities.

Characteristic features of most relaxation methods are high stability, when adequate relaxation factors are chosen, and relatively slow convergence, especially as the final solution is approached.

In order to increase the rate of convergence, Ishikawa and Hirata²⁸ introduced variable group relaxation factors, one for each component. Approximately the same computational procedure as Rose et al. was used with the exception of correcting these relaxation factors in each iteration. This was performed by using the difference between component flow rates entering and leaving the column. The method is claimed to be suitable for calculation of multicomponent distillation in complex columns. In spite of the correction of the relaxation factors the method is still rather time-consuming.

The relaxation method has been further modified by Jelinek et al.²⁹. They increased the rate of convergence by introducing different convergence-forcing procedures, such as the θ -method, which made it possible to use very high relaxation factors. The method was applied to complex columns and was further modified to handle interlinked columns³⁰.

Several other methods for distillation calculations which can not be classified into any of the three previous categories have been developed in recent years. A mathematically interesting method presented by Noh and Lee³¹ proposed that the modeling equations be considered as nonlinear finite difference equations. These were solved using the quasilinearization technique and iterating on imposed boundary conditions.

The method was further developed by Lee and Lee³² where the technique was applied to a complex column. The problems solved were rather simple and considered only systems exhibiting ideal vapor-liquid equilibrium.

Some methods deal with parametric study techniques, as for instance Jelinek et al.³³, where the change of an initial steady-state solution is studied by altering the value of a particular parameter, such as the reflux ratio. The methods take advantage of the initial available steady-state solution and thereby reduce the time required for obtaining a new steady-state solution compared to obtaining each solution independently.

A method applicable to design problems was presented by Ricker and Greens³⁴. It is based on successive approximation methods with adjustment of the number of equilibrium stages between iterations to satisfy given design specifications. The method is limited to simple distillation columns.

The current trend is to consider the distillation columns as a part of a chemical process rather than an isolated piece of equipment. The energy and mass balances are solved for the overall process by a flowsheeting program. A number of such programs are in use today, mainly in large companies, of which perhaps the most well-known is FLOWTRAN³⁵, owned by Monsanto Co.

Recently the flowsheeting program MULTICOL³⁶, which is limited to distillation calculations, was presented. The program is based on the work of Hutchison and Shewchuk²⁰.

The purpose of this work was to develop a computer program, DESTLA, for simulation of the steady-state behavior of general multicomponent distillation systems. It was decided that a modular approach to flowsheeting and thermodynamics should be used. Other desired specifications were:

- flexibility in defining the system and imposing constraints on its operation
- stable solution method to assure convergence for most calculation cases
- simple data input procedure
- comprehensive test of input data
- self-explanatory data output

- minimum use of computer storage and CPU time

Furthermore, the computer program should be constructed to allow the easy addition of modules other than those originally available and to be easily incorporated into similar computer programs for other separation processes, such as extraction.

2. DESIGN OF THE COMPUTER PROGRAM DESTLA

As stated in §1, the computer program DESTLA is based on a modular approach to distillation configurations. A unit cell comprising a number of unit operation modules is used for this purpose. By specifying the connection between various modules, flowsheets of arbitrary complexity may be assembled. All equipment and streams are designated by code numbers in the unit cell. The connections are easily specified in the computer program by giving the unit and stream number of both the source and destination. A complete description of the various pieces of equipment, available in the unit cell, and the constraints that may be imposed on them is given in §2.1-2.7.

Distillation calculations depend largely on physical and thermodynamic properties of the system. Phase equilibria data directly affect the extent of fractionation, while enthalpy data for vapor and liquid mixtures establish flow rates of both phases. Faulty or inaccurate data will thus yield unreliable results no matter how rigorous a solution technique is used. The relationships for phase equilibria and enthalpy used in DESTLA are chosen to accommodate most types of distillation problems likely to be encountered in the use of the program. As the thermodynamic models available in DESTLA can not represent all types of mixtures, a modular approach to thermodynamics is chosen, i.e. models for phase-equilibria and enthalpy may be easily replaced by models supplied by the user.

The flexibility offered by the modular approach, together with the many alternative constraints that may be imposed on the system necessitates a solution method that is numerically stable for a wide variety of different distillation problems. For this purpose, a plate-to-plate procedure was adopted in DESTLA. The main features of this solution method are simplicity, numerical stability, and ease of handling the different unit operation modules in a subroutine form. Furthermore, this method requires a minimum of computer storage as no matrix manipulations or partial derivative calculations are involved. The difficulties encountered in previous plate-to-plate methods, described in §1, are avoided by making conservation envelopes that include only single stages.

Iterative loops on each piece of equipment, such as bubble- and dew-

point calculations, are avoided as far as possible in order to decrease the time consumption. The temperature on each equilibrium stage is computed with use of a special subroutine ADJUST³⁷ which gives a rapid and assured convergence.

In order to facilitate the use of the computer program, special attention has been paid to the design of the routines dealing with input and output data. These routines were allowed to be quite extensive as they have a negligible computer time consumption compared to that used in the iterative calculations. The most critical interface between the user and the computer program is the input phase. In order to diminish the risk of feeding erroneous or incomplete data, all input data is comprehensively checked. Furthermore, all input data are echoed back to the user for further checking. In the output phase, the results from the calculations are printed out with explanatory text readily understood by the engineer.

DESTLA can presently handle up to 20 components and 99 plates, and auxiliary equipment, but can easily be extended by changing some of the dimensional statements in the program.

2.1 The unit cell

The unit cell, shown in appendix 1, consists of the following unit operation equipment:

plate; flash-drum; reboiler; partial condenser; total condenser; heat exchanger; mixing vessel for liquids; mixing vessel for vapors; liquid separation vessel.

The two digits on the right side of each piece of equipment represents its code number. A plate, for instance, has the code number 00. Vapor streams are represented by dashed lines, and liquid streams by full lines. All streams are numbered using positive figures for entering streams and negative figures for leaving streams.

In the unit cell some streams are entering and leaving at the corner of the unit as shown in figure 1. These streams are used either for cooling or heating purposes and are not mixed with the other streams in the unit. The heat transfer may also be provided directly (in kW) without using

any heating/cooling stream. Heat losses can also be handled.

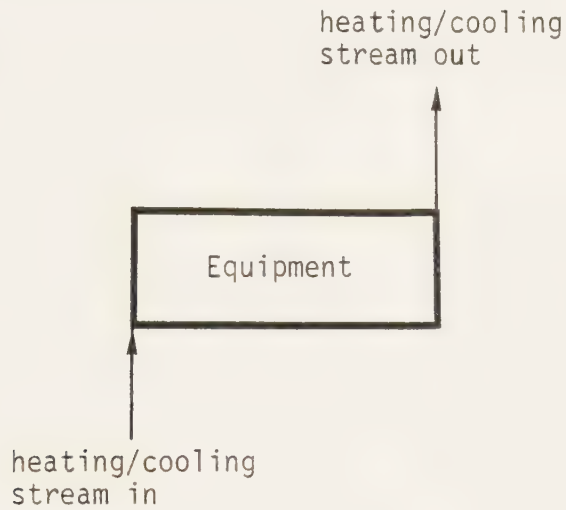


Figure 1. Definition of heating/cooling stream.

It is possible to withdraw a side stream from most modules in the unit cell as shown in figure 2. This is just a stream splitting, and hence the side stream has the same concentration and physical properties as the main stream.

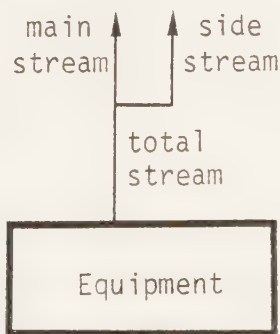


Figure 2. Definition of side stream.

The unit cell is designed to enable all connections within the distillation plant to be made solely with the aid of figure A1. Any leaving and entering streams may be connected together. The two streams may be either from the same unit cell or from two different unit cells. However, connections within a piece of equipment or between a vapor and a liquid stream are not permitted. Furthermore, connections between plates in the same distillation column are automatically established by the program. The streams no. 04 and -02 of the top plate and streams no. 02 and -04 of the bottom plate in a

column must always be connected to another piece of equipment.

A comprehensive description of the establishment of the connection matrix is given elsewhere³⁸.

Necessary external input streams, such as feed streams and heating/cooling streams, are accounted for merely by specifying the flow rate and properties for the actual stream. All entering streams, except for vapor stream 02 and liquid stream 04 entering a plate, may be used. In cases where stream 02 or 04 is to be used as external input stream, either a vapor mixing vessel (for stream 02) or a liquid mixing vessel (for stream 04) must be connected between the actual plate and the external stream. A more detailed description is given in the user's manual³⁸.

2.2 Plate

The liquid flow input (stream no. 04) always originates from the plate above, except for the top plate in a column, where it must be connected to another piece of equipment. Similarly, the vapor flow input (stream no. 02) always originates from the plate below, except for the bottom plate.

A third stream can be introduced on a plate, namely the feed (stream no. 01). According to figure A1 the vapor portion of the feed is added to the vapor rising from the plate below and the liquid portion to the liquid coming from the plate above the feed plate. Perfect mixing is assumed in both cases. If the plate is assumed to behave ideally, vapor stream no. -02 and liquid stream no -04 will leave the plate at equilibrium. These streams may be split so that vapor and liquid side streams (streams no. -03 and -05) can be withdrawn from the plate. The latter streams are then assumed to have the same composition and conditions as the inter-stage streams from which they are drawn.

The ideal plate can be extended to a real plate which accounts for mass transfer efficiencies by using a Murphree plate efficiency.

The plate may be heated, either with vapor stream no. 07 or liquid stream no. 06, or cooled, with liquid stream no. 06. The heating or

cooling stream leaves the plate as liquid stream no. -06. If the cooling stream should be vaporized it can be withdrawn as vapor stream (no. -07). The heat transfer may also be provided explicitly without using any heating/cooling stream. Heat losses and pressure drop across the plate can also be handled.

2.3 Flash-drum, reboiler and partial condenser

The stream configurations around a flash-drum, a reboiler and a partial condenser are quite similar. A liquid stream is used as flow input to a flash-drum and a reboiler while a vapor stream is used for a partial condenser. These units are assumed to function as ideal equilibrium stages yielding a vapor and a liquid stream at equilibrium.

For a flash-drum, the pressure must always be specified. If isothermal flashing is to be simulated, the temperature must also be given. In cases where neither temperature, for isothermal flashing, nor heat transfer data are given, the program will automatically assume adiabatic flashing.

The amount of liquid vaporized in a reboiler, or vapor condensed in a partial condenser, can be specified in DESTLA according to one of the following alternatives:

1. fraction of inlet stream to be vaporized/condensed
2. product flow rate (i.e. bottom and distillate streams respectively)
3. heat transfer, either explicitly (in kW) or as a heating/cooling stream (i.e. stream no. 19 for a reboiler and stream no. 24 for a partial condenser)

It should be noted that the third alternative is not applicable when the assumption of constant molar flows is used in the computations.

2.4 Total condenser

The flow input to the total condenser, vapor stream no. 26, is cooled and withdrawn as liquid stream no. -27. The enthalpy of the liquid depends on the amount of heat removed and may be specified in either one of the following ways:

1. degree of subcooling
2. heat removed, either explicitly or as a cooling liquid (stream no. 29).
The cooling stream is withdrawn as either liquid (stream no. -29) or vapor (stream no. -30), if being vaporized.

Only the first alternative is applicable in the case of constant molar flows.

In cases where none of the above alternatives are used the liquid will be assumed to be at its bubble-point temperature.

2.5 Heat exchanger

The heat exchanger is assumed to be of counter-current type. On the hot side, the flow input consists of either liquid stream no. 35 or vapor stream no. 37. The heating medium leaves the heat exchanger as liquid stream no. -35. The flow input to the cold side consists of liquid stream no. 31 and leaves the heat exchanger as liquid stream no. -31 or, if being vaporized, as vapor stream no. -33.

In cases where a liquid or vapor stream is needed at a specific temperature, it is possible to use only one side of the heat exchanger and specify the outlet temperature. Thus the other side of the heat exchanger as well as the overall heat transfer coefficient and heat transfer area are not considered.

2.6 Mixing vessels

In these vessels a pair of either liquid or vapor streams are mixed together, yielding one outlet stream.

In cases where heat of mixing is considered, the mixing of two liquids, at or near their bubble-point temperature, may result in partial vaporization. The vapor thus formed is assumed to be at equilibrium with the outlet liquid and is withdrawn as stream -40. Analogously, liquid stream no. -44 is withdrawn from the vapor mixing vessel in case of partial condensation.

The mixing vessels may also be used for flow-splitting purposes. In that case only stream 38, for a liquid mixing vessel, and stream 42, for a vapor mixing vessel, is used as input and can be split into streams -38 and -39 or streams -42 and -43 respectively.

Furthermore, the mixing vessels may be utilized to change the pressure of a liquid or vapor mixture. In this case only stream 38 (or 42) is used as input and stream -38 (or -42) as outlet.

2.7 Separation vessel for liquids

For liquid mixtures with partial miscibility, liquid stream no. 46 is split into two liquid phases at equilibrium. The "lighter phase" is assigned in DESTLA as the phase which is most rich in the light component and is withdrawn as stream no. -46. Outlet stream no. -48 will thus represent the "heavier phase".

In cases where no phase splitting occur, the inlet stream will be divided into two equal parts having the same composition as the inlet stream.

3. MODELING THE EQUIPMENT OF THE UNIT CELL

A computer program for simulating the steady-state of a general distillation configuration requires a set of equations that accurately represent mass and energy balances and thermodynamic requirements of the units involved in the configuration. Furthermore, a suitable solution method for solving these equations must be selected. Mass and energy balance equations used for modeling the various unit operation modules in DESTLA are fundamental and may be found in several textbooks. However, these equations are presented below to facilitate the description of the solution method used. The equations are outlined for a plate but can be applied to any of the other equipment with slight modifications.

3.1 Plate modeling

The model plate for mathematical simulation is shown in figure 3. The plate has one feed stream, F_j , one vapor side-stream, VS_j , and one liquid side-stream, LS_j . Heat, Q_j , can be added to or removed from the plate, to simulate intermediate heating or cooling, respectively. Furthermore, heat losses, QL_j , can be accounted for.

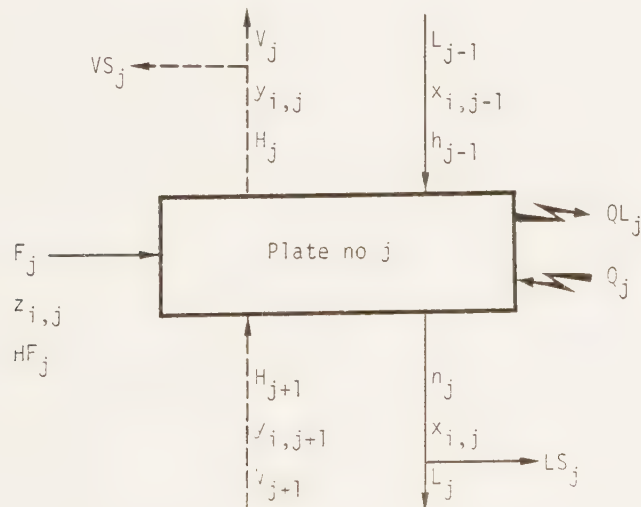


Figure 3. Model plate.

The basic equations used in the simulation are derived by making material and heat conservation envelopes encircling the plate. An overall mass balance yields:

$$(V_j + VS_j) + (L_j + LS_j) = F_j + V_{j+1} + L_{j-1} \quad (1)$$

A component mass balance for component i may be expressed as:

$$\begin{aligned} (V_j + VS_j) \cdot y_{i,j} + (L_j + LS_j) \cdot x_{i,j} &= \\ = F_j \cdot z_{i,j} + V_{j+1} \cdot y_{i,j+1} + L_{j-1} \cdot x_{i,j-1} \end{aligned} \quad (2)$$

A heat balance gives:

$$\begin{aligned} (V_j + VS_j) \cdot H_j + (L_j + LS_j) \cdot h_j &= \\ = F_j \cdot HF_j + V_{j+1} \cdot H_{j+1} + L_{j-1} \cdot h_{j-1} + Q_j - QL_j \end{aligned} \quad (3)$$

The term Q_j is assumed to be positive if heat is added to the plate and negative if heat is removed, while the heat loss term, QL_j , is always assumed to be positive.

The remaining basic equations are the summation equations on plate j :

$$\sum_{i=1}^c y_{i,j} = \sum_{i=1}^c x_{i,j} = 1.0 \quad (4)$$

and the vapor-liquid equilibrium relationship:

$$y_{i,j} = K_{i,j} \cdot x_{i,j} \quad \text{for } 1 \leq i \leq c \quad (5)$$

The equilibrium constant, $K_{i,j}$, is generally a function of pressure, temperature, and vapor and liquid compositions;

$$K_{i,j} = K(P_j, T_j, \bar{x}_j, \bar{y}_j) \quad (6)$$

where $\bar{x}_j$ and $\bar{y}_j$ stand for $x_{1,j}, x_{2,j}, \dots, x_{c,j}$ and $y_{1,j}, y_{2,j}, \dots, y_{c,j}$, respectively.

Similarly, vapor and liquid enthalpies are functions of the fluid state;

$$h_j = h(P_j, T_j, \bar{x}_j) \quad (7)$$

$$H_j = H(P_j, T_j, \bar{y}_j) \quad (8)$$

The equilibrium and enthalpy relationships used in DESTLA are treated in more detail in §6.

According to the unit cell configuration (see A1) heat may be transferred to plates, flash-drums, reboilers, and condensers using external heating/cooling streams. This is especially significant for reboilers and condensers. Computation of heat transferred, Q_j , to such equipment is based on the following equations:

$$Q_j = F_{I,j} \cdot (H_{IN,j} - H_{OUT,j}) \quad (9)$$

and

$$Q_j = K \cdot A \cdot \Delta T_{LM} \quad (10)$$

where

K = overall heat transfer coefficient

A = heat transfer area

ΔT_{LM} = logarithmic mean value of temperature difference between stage temperature and inlet and outlet temperatures of heating/cooling stream.

The symbols used in equation (9) refer to figure 4 below. The enthalpies of the heating/cooling stream are computed with equation (7) or (8) for liquid and vapor mixtures respectively.

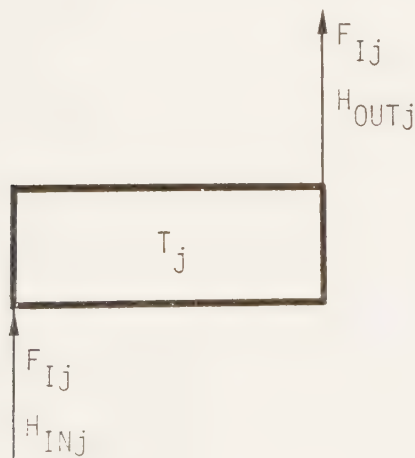


Figure 4. Symbols used for heating/cooling streams.

In order to extend the ideal plate to a real plate which accounts for mass transfer efficiencies the Murphree plate efficiency is used. This

is defined for plate j by

$$E_{i,j} = \frac{y_{i,j} - y_{i,j+1}}{y_{i,j}^* - y_{i,j+1}} \quad (11)$$

The quantity $y_{i,j}^*$ is obtained from equation (5) where $K_{i,j}$ is evaluated at the bubble-point temperature for the liquid leaving plate j . On a given plate, a total number of $(c-1)$ independent efficiencies may be specified, although the most common choice is to use the same efficiency for all components.

3.2 Modeling of auxiliary equipment

The auxiliary equipment is simulated by the same equations used for the plate with slight modification of the mass and energy balances. The necessary equations for the various types of equipment are tabulated below:

<u>Equipment</u>	<u>Necessary equations</u>	<u>Zero streams</u>
Flash-drum	(1) - (12)	V_{j+1}, L_{j-1}
Reboiler and Partial condenser	(1) - (12)	V_{j+1}, L_{j-1}
Total condenser	(1), (2), (7) - (10)	$V_{j+1}, L_{j-1}, (V_j + VS_j)$
Heat exchanger	(1), (2), (9), (10)	$V_{j+1}, L_{j-1}, (V_j + VS_j)$
Mixing vessel	(1) - (8)	$V_{j+1} \text{ (or } L_{j-1})^*, Q_j, QL_j$
Separation vessel	(1), (2), (4), (12), (13)	V_{j+1}, L_{j-1}

*The terms V_{j+1} and L_{j-1} in equations (1) - (3) will vanish in the case of mixing vessels for liquids and vapors respectively.

For reboilers and partial condensers the duty may be specified either in the same way as for a plate or implicitly by setting a value for the L_j/V_j ratio or the flow rate of the product stream. In the two latter cases equation (3) is not required unless the amount of heat transferred, Q_j , is to be simulated.

The equations (1), (2) and (9) modeling the heat exchanger are used for

both the hot and cold side of the heat exchanger.

For mixing vessels, the mass and energy balances are sufficient for most cases. However, in order to include the possibility of crossing the saturation line, when mixing two fluids at or near the saturation condition, the model has been extended to include the equilibrium relationship.

The separation vessel for liquids is limited in DESTLA to isothermal operation. For the mathematical modeling, equations (1), (2) and (4) are used. The mass balances are used with F_j as the entering liquid stream, $(V_j + VS_j)$ as the light phase and $(L_j + LS_j)$ as the heavy phase. The equilibrium relationship used is

$$y_{i,j} \cdot \gamma_{i,j}^L = x_{i,j} \cdot \gamma_{i,j}^H \quad \text{for } 1 \leq i \leq c \quad (12)$$

where $y_{i,j}$ and $x_{i,j}$ are the mole fractions of component i in the light phase and heavy phase respectively. The activity coefficients, $\gamma_{i,j}$, are in general functions of temperature and liquid composition while pressure dependence may often be neglected; thus

$$\gamma_{i,j} = \gamma(T_j, \bar{x}_j) \quad (13)$$

The computation of activity coefficients is treated in some more detail in §6.1.

4. SOLUTION METHOD AND CONVERGENCE CRITERIA

4.1 Solution method

The solution of a steady-state distillation problem requires that model equations are simultaneously satisfied for all pieces of equipment involved in the configuration. Most of the equations used are non-linear, and even for few-stage problems the equation system becomes too complex to allow an explicit solution. Thus an iterative solution method is always necessary.

The first decision in formulating a solution method is whether the model equations should be grouped by type or by stages. According to Friday and Smith¹⁸ most methods use the first alternative and each type of equation would be solved simultaneously for all stages. In the second alternative, all equations could be solved either simultaneously, as for instance with the method of Naphtali and Sandholm^{2,3} or by a plate-to-plate procedure. The latter procedure is chosen in DESTLA as it is a very simple method and easily allows the unit operation modules to be in a subroutine form.

There are basically two alternative approaches to generating stage compositions in the plate-to-plate method. One of these utilizes conservation envelopes that include a product stream from the distillation column, i.e. distillate or bottom. This procedure presents difficulties due to round-off errors and is especially unstable for complex columns. The other approach, which is used in DESTLA, is based on conservation envelopes that encircle only single stages. This method is more stable as it uses only streams entering the conservation envelope to calculate outlet streams.

The computational procedure for a typical plate is performed according to the following four steps:

Step 1 Computation of the vapor and liquid flow rates using equations (1) and (3). Flow rate and properties of all entering streams are known. These are assigned either exact values, for streams defined in input data, or the last computed values, for connected streams. The enthalpy of leaving streams, to be used in equation (3), are values from the preceding iteration.

Step 2 Solution of equations (2) and (5) for liquid and vapor mole fractions. In cases where non-ideal plates are used, equation (11) is included in the previous equations. The equilibrium constants in equation (5) are computed from equation (6) using temperature and compositions from the preceding iteration.

Step 3 A new temperature is assumed using equation (4) together with a suitable relaxation factor according to:

$$(T_j)_n = (T_j)_{n-1} + \left(\sum_{i=1}^C x_{i,j} - 1.0 \right)_n \cdot (R_j)_n \cdot (T_j)_{n-1} \quad (14)$$

The relaxation factor, R_j , is obtained from ADJUST³⁷, an adaptive convergence algorithm for general trial and error computations. Using temperatures from the two preceding iterations, ADJUST calculates an optimal relaxation factor. When the sum of mole fractions is equal to unity there will be no change in temperature. This temperature will be equal to the bubble-point temperature.

Step 4 Liquid and vapor compositions are normalized and new enthalpies are computed for outlet streams using equations (7) and (8).

In cases where heat transfer occurs, equations (9) and (10) must be solved before computing the flow rates in step 1. The energy balance (equation 9) may be solved in many alternative ways depending on the type of input specifications made. The outlet stream temperature may be specified explicitly, or implicitly, by requiring the outlet stream to be at its saturation point. Furthermore, the duty may be specified indirectly by setting a value for the overall heat transfer coefficient and heat transfer area.

The computational procedure above is in principle valid for all components of the unit cell, although there are slight variations.

The above steps involve no iterative calculations. For equilibrium stages, this means that some of the equations are not satisfied after normalizing the compositions unless the computed sum of mole fractions is unity. Satisfying all equations would certainly require time consuming iterations. This is not worth-while, as the solution would be based on flow rates and conditions of the entering streams that are not final. The only piece of equipment for which iterative computation to full convergence is used each time is the separation vessel for liquids. These com-

putations are much more time consuming than for the other units and are thus performed only every fifth iteration.

The computations are performed for each unit in the same order as they appear in the unit cell, i.e. firstly all plates in consecutive order, and, lastly, the separation vessel. Then the computation sequence is reversed starting with the equipment having the highest code number and ending with plate no 1. After these two computation sequences, which constitute one iteration, a test is made to check whether the convergence criteria are satisfied. If they are not satisfied a new iteration is performed. The tests of convergence are described in § 4.2.

4.2 Convergence criteria

The most logical convergence test to choose in distillation calculations is perhaps the bubble-point check. Many distillation methods base the convergence test on this criterion. It was found, however, both during this work and by many other authors, as for instance Gentry³⁹, that this check is not sufficiently restrictive. This is particularly noticeable when dealing with strongly non-ideal mixtures. In such cases, a satisfactory bubble-point check may be obtained without being near the final solution.

The bubble-point check in DESTLA is therefore complemented with a test on the component flow rates. Two criteria have then to be fulfilled. The bubble-point check can be stated as follows

$$\left| \sum_{i=1}^C (K_{i,j} \cdot x_{i,j}) - 1.0 \right| \leq \epsilon_1 \quad \text{for all ideal stage units } 1 \leq j \leq N \quad (15)$$

The second test is based on the component mass balance of the distillation column where the sum of component flow rates for entering streams are compared with those for leaving streams. This test is performed according to the following equations, see figure 5 below.

$$|(IN_i - OUT_i)/IN_i| \leq \epsilon_2 \quad \text{for } 1 \leq i \leq C \quad (16)$$

where

$$IN_i = V_{N+1} \cdot y_{i,N+1} + L_0 \cdot x_{i,0} + \sum_{j=1}^N (F_j \cdot z_{i,j}) \quad (17)$$

and

$$OUT_i = V_1 \cdot y_{i,1} + L_N \cdot x_{i,N} + \sum_{j=1}^N (VS_j \cdot y_{i,j} + LS_j \cdot x_{i,j}) \quad (18)$$

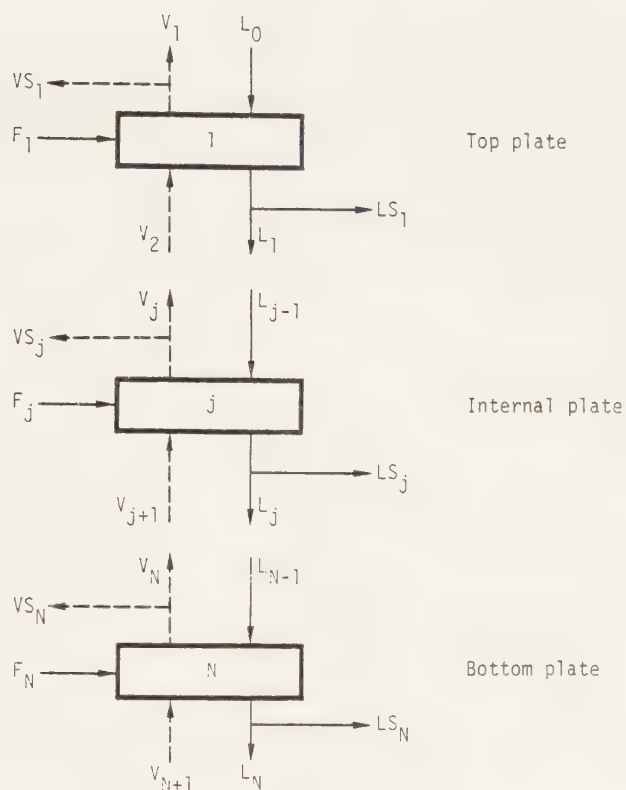


Figure 5. Schematic representation of model column used in the convergence check.

The tolerance error ϵ_1 is to be specified by the user while ϵ_2 is set by the program. A standard value for ϵ_2 is 0.001, i.e. 0.1 % error in the component flow rates.

These two convergence criteria proved to be restrictive enough to ensure a satisfactory solution.

5. PROGRAM OPERATION

The equations utilized in modeling the equipment available in the unit cell are incorporated into the executive computer program DESTLA for determining the steady-state solution of general distillation plants. The computer program, written in FORTRAN IV, consists of the main program and 52 subroutines comprising about 4300 punch cards and 44 800 decimal words of core memory. A schematic flow diagram of the executive program is shown in figure 6. The various steps of the flow diagram are briefly outlined below.

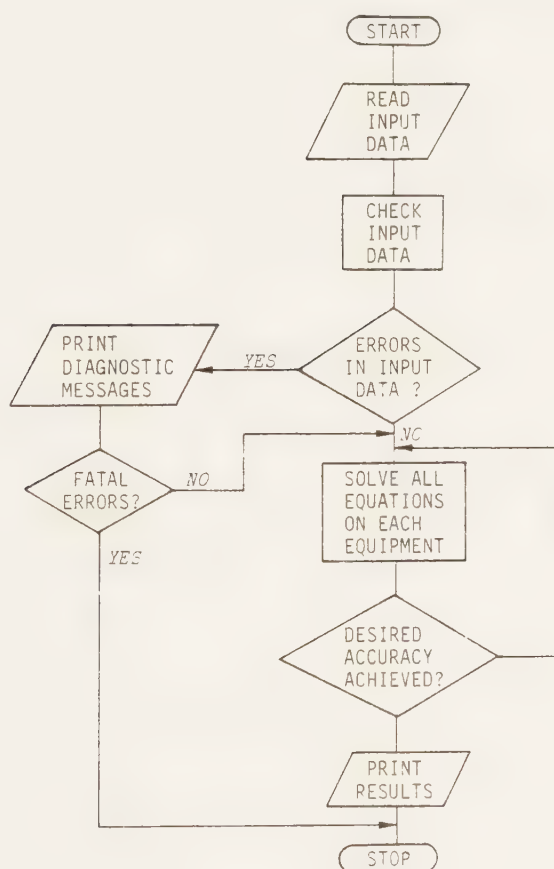


Figure 6. Schematic flow diagram of the computer program.

5.1 Input of data

The necessary input data for an execution of DESTLA consists mainly of the flowsheet, component data, data for all incoming streams, heat transfer data and special data for the various pieces of equipment. The flowsheet is described by specifying the destination and source of all

streams connecting two pieces of equipment.

Component data comprises data for the computation of vapor-liquid equilibrium, liquid-liquid equilibrium and enthalpy of liquid and vapor mixtures. This data may be specified either for the models readily available in DESTLA or for external thermodynamic packages supplied by the user. A description of the treatment of equilibrium and enthalpy is given in § 6.

For all incoming external streams, i.e. streams not originating from other equipment within the flowsheet, the flow rate and properties must be specified. For outlet streams, any flow splitting must be specified.

Heat transfer data comprises the amount of heat transferred, heat losses, overall heat transfer coefficient and heat transfer area. This data may be specified for all heat transfer equipment within the unit cell.

Murphree plate efficiencies, pressure drop across a plate, reflux ratios and reboiler and condenser duties are some examples of special data that may be specified for various units.

A comprehensive description of the data input procedure is given in a separate user's manual³⁸.

5.2 Input data testing and diagnostic messages

The input data are tested in order to diminish the risk of feeding DESTLA with erroneous or incomplete data. All input data, except those concerned with the connection matrix, are echoed in a print-out to further facilitate the detection of errors. If an error is detected during this phase of program operation, a self-explanatory message is printed out. If the error is fatal the run is terminated, but if it is not serious a warning message is printed out and the run is continued.

The validity of each connection is checked and if a nonexisting cell number or a prohibited connection is used, a diagnostic message is printed out. Two examples of these messages are given below.


```
****ERROR IN CONNECTION MATRIX* THE STREAM NUMBER -01 IS NOT ALLOWED****  
****ERROR IN CONNECTION MATRIX* STREAM NUMBER 14 OF CELL NUMBER 10 IS  
CONNECTED TWICE****
```

After being checked, connection codes are printed out as a connection matrix and replaced by internal numerical designations.

Component data are subsequently tested by computing equilibrium constants and enthalpy data for mixtures of various compositions. If any negative values are found, a diagnostic message is printed out. In the same message, information is given as to whether the user has used own subprograms or not. A typical error message is shown below.

```
****ERROR IN KVAL (SUPPLIED BY THE USER)****
```

The same diagnostic message would be printed out if the user used an external subprogram for phase equilibria but forgot to link it to DESTLA.

The remaining input data, such as specification of entering streams, heat transfer data and special data for various equipment, are then checked to ensure that no obvious errors occur. For instance flow rates, pressures, temperatures (absolute) and concentrations are tested so that no negative values occur. Furthermore, the sums of mole fractions are checked to be 1.0 and the value of plate efficiencies should be within the normal range 0 to 100 %. Some of the typical diagnostic messages for errors in such data are given below.

```
****ERROR THERE IS A NEGATIVE PRESSURE****
```

```
****ERROR THE SUM OF MOLE FRAC IS LESS THAN 1.0****
```

```
****WARNING THERE IS A PLATE EFFICIENCY GREATER THAN 100 %****
```

5.3 Calculations

If no errors have been detected in the input data, the iterative calculations are started. The pieces of equipment are computed in the same order as they appear in the unit cell, starting with all plates, in consecutive order, and finishing with the separation vessel for liquids. Afterwards, the computation sequence is reversed, starting with the piece

of equipment having the highest code number and finishing with plate no 1. These two computation sequences constitute one iteration.

During the computation for each piece of equipment, the flow rate and properties of all streams entering the equipment are assumed to be known, although approximately if connected to another piece of equipment. The physical properties of all leaving streams are also treated as known variables. Thus the flow rate and composition for the leaving streams can easily be computed. A new estimate of the temperature is made, for ideal stage equipment, using a special convergence algorithm.

All calculations for each unit are made non-iterative, as far as possible, in order to reduce time consumption. Computations for liquid separation vessels are, however, iterative since convergence is required in each iteration.

Each iteration is followed by a convergence test. If convergence is not achieved, a new iteration is performed.

5.4 Output of data

When convergence is achieved, the iterative calculations are interrupted and the computed results are printed out. The output consists of all important information; both computed and provided as input data, for each piece of equipment in the distillation configuration. First, information concerning each plate is printed out consecutively followed by the other equipment in the same order as it appear, in the unit cell configuration. The information consists of flow rate, pressure, temperature, heat content and composition of all streams entering and leaving the equipment. Furthermore, such data as plate efficiency, heat transfer, heat losses, heat transfer coefficient, heat transfer area, reflux ratio, and reboiler duty for the various units are printed out. Finally the time consumption for the input and pre-calculations, unit cell calculations and output and post-calculations are listed.

The output data are printed in fully written-out text to facilitate the evaluation of the results by the user. An example of a typical output from DESTLA is shown in appendix 2 for a plate, a reboiler and a total condenser.

In cases where the maximum allowed CPU-time consumption, fixed by the user, is exceeded, the execution is interrupted and the following message is printed out:

****MAXTIME EXCEEDED****

This message is followed by a print out of the sum of vapor mole fractions on each plate at the time of interruption. Then the results obtained are printed out in the same format as described above.

6. TREATMENT OF PHASE EQUILIBRIA AND ENTHALPY

When simulating the steady-state behavior of a distillation column the phase equilibrium relationships are the most important features which directly affect the composition profile, while the enthalpy relationships are essential for the internal column flow rates. Thus a rigorous solution requires accurate vapor-liquid, and in some cases liquid-liquid, equilibrium data as well as detailed enthalpy data for both vapor and liquid mixtures. In cases where enthalpy data is lacking, a less rigorous, but nevertheless satisfactory solution, concerning concentration profiles can be obtained by assuming constant molar heats of vaporization. On the other hand, a lack of equilibrium data can in a few cases be approximated by assuming ideal vapor and liquid mixtures, but for most cases this approximation will yield very inaccurate results. Consequently, during the development of DESTLA more emphasis has been focused on investigating phase-equilibria rather than enthalpy relationships.

6.1 Phase equilibria models

The equilibrium constant, K_i , is defined by equations (5) and (6) where it is seen to be a function of pressure, temperature and composition. It can be further expressed by the following, completely general and rigorous equation:

$$K_i = \frac{\gamma_i f_i^{OL}}{P \phi_i} \quad (19)$$

where γ_i is the activity coefficient for component i in the liquid phase, f_i^{OL} is the fugacity of pure liquid i and ϕ_i is the fugacity coefficient for component i in the vapor-phase. All terms are for the actual system temperature and pressure.

For moderate pressures, except in systems exhibiting strong chemical interactions, the above expression may be approximated with:

$$K_i = \frac{\gamma_i P_i^0}{P} \quad (20)$$

This last equation is used in DESTLA for the computation of equilibrium constants, but may easily be replaced by other models. It is based on the

assumption of ideal behavior of the vapor phase, while non-ideality of the liquid phase is accounted for by the activity coefficient γ_i .

The vapor pressures of pure components are calculated using the well-known Antoine equation:

$$\log P_i^0 = A_i - B_i / (C_i + t) \quad (21)$$

The constants A_i , B_i and C_i for many substances can be found in some text books, for instance reference (40).

There has been a great number of equations proposed in the literature for calculating the activity coefficient, γ_i , and a large number have survived primarily because no single equation has been proposed which can represent all types of liquid solutions. In DESTLA the activity coefficients are calculated by either the Wilson equation⁴¹

$$\ln \gamma_k = 1 - \ln \left[\sum_{j=1}^c x_j \Lambda_{kj} \right] - \frac{\sum_{i=1}^c \frac{x_i \Lambda_{ik}}{\sum_{j=1}^c (x_j \Lambda_{ij})}}{\quad} \quad (22)$$

or the recently developed UNIQUAC model⁴² which consists of the following equations:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad i = 1, 2, \dots, c \quad (23)$$

combin. residual

where

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\Theta_i}{\phi_i} + \zeta_i - \frac{\phi_i}{x_i} \sum_{j=1}^c x_j \zeta_j \quad (24)$$

and

$$\ln \gamma_i^R = q_i \left\{ 1 - \ln \left(\sum_{j=1}^c \Theta_j \tau_{ji} \right) - \frac{\sum_{j=1}^c \frac{\Theta_j \tau_{ij}}{\sum_{k=1}^c \Theta_k \tau_{kj}} \right\} \quad (25)$$

$$\zeta_i = \left(\frac{z}{2} \right) (r_i - q_i) - (r_i - 1) \quad ; \quad z = 10$$

$$\Theta_i = \frac{q_i x_i}{\sum_{j=1}^c q_j x_j} \quad ; \quad \Phi_i = \frac{r_i x_i}{\sum_{j=1}^c r_j x_j}$$

$$\tau_{ij} = \exp\{-(u_{ij} - u_{jj})/RT\} \quad (26)$$

The latter model gives the activity coefficients in terms of a combinatorial part, essentially due to differences in molecular sizes and shapes, and a residual part, essentially due to molecular interactions.

The binary interaction parameters, Λ_{ij} in the Wilson equation and $(u_{ij}-u_{jj})$ in the UNIQUAC equations, are tabulated for many systems by Gmeling and Onken⁴³. When no parameters are to be found in the literature, they could be determined from experimental equilibrium data with use of EQUIL⁴⁴, a computer program for calculating and plotting vapor-liquid equilibria. In the absence of experimental data for a given system, the UNIFAC group contribution method⁴⁵ could be used for predicting activity coefficients in non-electrolyte liquid mixtures. The UNIFAC model is also adopted in the computer program EQUIL.

The distribution of components between two immiscible liquid phases is computed according to:

$$\frac{x_i^I}{x_i^{III}} = \frac{\gamma_i^{II}}{\gamma_i^I} \quad (27)$$

In this case, the activity coefficients are always computed with the UNIQUAC model, as the Wilson equation is inapplicable to liquid mixtures with partial miscibility.

Many other models for the computation of vapor-liquid and liquid-liquid equilibria are encountered in the literature. For instance, for hydrocarbon systems the equilibrium constant is often expressed as a polynomial function of temperature⁵. Other more complicated models may be used for systems exhibiting chemical reactions, such as water-formaldehyde⁴⁶. Furthermore, even when using equation (20) there are a great number of models for calculating activity coefficients to choose from. To provide for all users' special requirements, the equilibrium package

is made replaceable. The user may thus use self-supplied subprograms which should be written according to the description in the user's manual³⁸.

6.2 Enthalpy models

The solution of heat balances requires enthalpy data for liquid mixtures at temperatures up to the bubble-point and for vapor mixtures at or above the dew-point temperature.

Liquid enthalpy

The bubble-point enthalpy of a liquid mixture is given by the relationship

$$h_l = \sum_{i=1}^C h_{li}^0 \cdot x_i - RT^2 \sum_{i=1}^C x_i (\partial \ln \gamma_i / \partial T)_{P,x} \quad (28)$$

The first term on the right-hand side represents the ideal mixing enthalpy and the other term represents the heat of mixing.

For the evaluation of the heat of mixing, experimental data are required at different temperatures for all the components in the mixture. Since for most systems there will be a lack of such data, the model for computation of enthalpy for liquid mixtures to be used in DESTLA was simplified to

$$h_l = \sum_{i=1}^C h_{li}^0 x_i \quad (29)$$

The enthalpies for the pure components are calculated from the relationship

$$h_{li}^0 = C_{pi} \cdot (t - t_{ref}) ; \quad t_{ref} = 0^\circ\text{C} \quad (30)$$

where the specific heat of liquids, C_{pi} , is a polynomial function of temperature, T , according to

$$C_{pi} = a_{1i} + a_{2i}T + a_{3i}T^2 + a_{4i}T^3 + a_{5i}T^4 \quad (31)$$

In cases where constant molar heats of vaporization are assumed, the bubble-point enthalpies of liquid mixtures are set equal to zero.

Vapor enthalpy

In DESTLA, the dew-point enthalpies of vapor mixtures are computed from the relationship

$$H_V^S = h_l + \Delta H_V \quad (32)$$

where the molar heat of vaporization, ΔH_V , is obtained from

$$\Delta H_V = \sum_{i=1}^C \Delta H_{V,i}^0 y_i \quad (33)$$

and

$$\Delta H_{V,i}^0 = b_{1i} + b_{2i}T + b_{3i}T^2 + b_{4i}T^3 + b_{5i}T^4 \quad (34)$$

The enthalpies of super-heated vapor mixtures are calculated from

$$H_V = H_V^S + \sum_{i=1}^C y_i C_{pgi} (t - t_d) \quad (35)$$

where t_d is the dew-point temperature of the mixture. The specific heat of vapor, C_{pgi} , is related to temperature in the same way as was the specific heat of liquids.

In cases where constant molar heats of vaporization are assumed, the dew-point enthalpies of vapor mixtures are set equal to unity and the enthalpy of mixtures may be calculated according to:

$$H = 1.0 - \frac{\text{energy to convert 1 mole of mixture to saturated vapor}}{\text{molar heat of vaporization}}$$

This yields for

subcooled liquids	$H < 0$
saturated liquids	$H = 0$
partially flashed mixture	$0 < H < 1$
saturated vapor	$H = 1$
superheated vapor	$H > 1$

The models for calculation of enthalpies are replaceable and thus give the user the possibility to include the heat of mixing for liquid mixtures.

7. COMPUTED EXAMPLES

Many different types of test problems involving multicomponent distillation have been successfully solved with DESTLA. The computed examples outlined below comprise distillation columns with multiple feeds and sidestreams, multicolumn flowsheets, mixtures exhibiting strongly non-ideal vapor-liquid equilibria and wide-boiling mixtures.

In order to illustrate the computational ability of DESTLA, four numerical examples are given. The convergence criteria parameters (defined in § 4.2) used in these problems were $\epsilon_1 = 0.00001$ and $\epsilon_2 = 0.001$. The problems are solved on the UNIVAC 1108 computer system at the Lund Data Center.

7.1 Example 1

In this example a mixture of phenol and cresols is to be separated. The system is considered to exhibit ideal behavior, and the equilibrium constants are computed using only the Antoine equation. Furthermore, constant molar flow rates are assumed. The Antoine parameters, obtained from Boublik et al.⁴⁰, are presented in table A3.1. A large number of plates are required for the separation as phenol and o-cresol have nearly the same volatility ($\alpha \approx 1.29$). A distillation tower operating at a total pressure of 13.3 kPa and containing 50 ideal plates was chosen. The distillation tower (see schematic flowsheet below) is equipped with a partial condenser and a reboiler. A saturated liquid feed of 34 mole-% phenol, 27 mole-% o-cresol, 16 mole-% p-cresol, and 23 mole-% m-cresol is introduced to the 26th plate (from the top) at a rate of 100 kmol/h. The reflux ratio is set to 10 and the distillate rate is 34 kmol/h.

With these specifications, the converged solution required about 100 seconds of CPU time. Initial, intermediate, and final liquid concentration profiles for phenol, obtained during the computation, are plotted in figure A4.1.

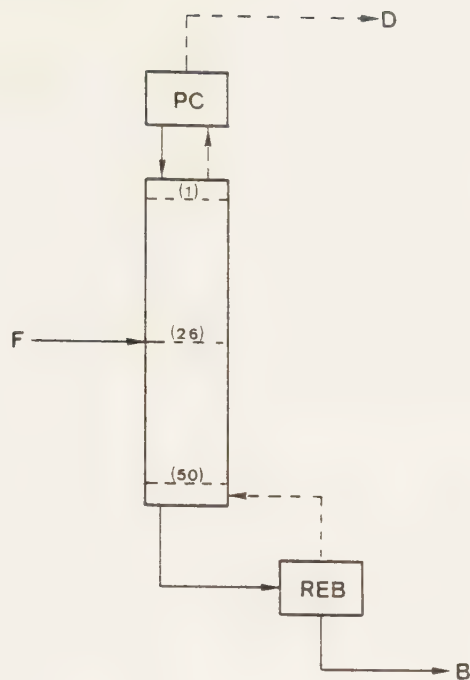


Figure 7. Schematic column configuration for example 1.

7.2 Example 2

In this example a ternary system consisting of methanol, isopropanol and toluene was investigated. This system exhibits strongly non-ideal thermodynamic behavior, which can be seen from table A3.2 where the activity coefficients at infinite dilution as well as the azeotropic data for the three binary systems involved are given. The activity coefficients were calculated using the Wilson equation. Wilson's parameters and Antoine's constants for this system were obtained from Håla et al.⁴⁷ and are listed in table A3.3.

The distillation tower used in this example consists of 20 ideal plates and is equipped with a reboiler and a total condenser. A saturated liquid feed, consisting of 60 mole-% methanol, 30 mole-% isopropanol and 10 mole-% toluene, is fed to the seventh plate (from the top) at a rate of 100 kmol/h. The reflux ratio was specified at 2.0 and the flow rate of bottom product was set at 30 kmol/h. Constant molar flow rates were assumed.

The resulting liquid composition profiles for methanol and toluene are shown in figure A4.2. About 9.5 kmol/h of toluene is withdrawn as distillate although toluene is the component with the highest boiling point in this system. This is caused by the methanol-toluene azeotrope. The com-

position of the distillate is in fact very near the azeotropic value listed in table A3.2.

This example was also computed assuming ideal vapor-liquid equilibrium, i.e. the Wilson parameters were set equal to 1.0. The computed liquid compositions are plotted in figure A4.2 for comparison. This assumption of ideal behavior erroneously shows that almost all toluene is withdrawn as bottoms (> 9.99 kmol/h).

The CPU-time required for this fractionation problem was about 110 and 30 seconds for the non-ideal and ideal behavior, respectively. About 35 % of this time was consumed in vapor-liquid equilibrium computations.

7.3 Example 3

As an example of interacting columns, the Petlyuk towers for separation of ternary mixtures, using only one reboiler, are taken as the third example. The flowsheet is given in figure 8 below. A two-phase stream consisting of 30 % liquid is fed to the fourth plate of tower 1 which contains a total of 7 ideal plates. The feed consists of 40 mole-% hexane, 30 mole-% octane and 40 mole-% decane. The second tower has 15 ideal plates and is provided with a reboiler and a total condenser. From this tower the sidestreams LS_{10} , LS_{14} , and VS_{20} , are withdrawn. These are set to 50, 30, and 40 kmol/h respectively. The flow rate of the bottom product (B) was specified as 30 kmol/h and the reflux ratio was set to 3.0. Both towers operate at 101.3 kPa. The ternary system is considered to behave ideally and the vapor-liquid equilibrium constants were calculated using the Antoine equation for component vapor pressures. The Antoine parameters were obtained from Boublik⁴⁰ and are tabulated in table 3.4.

The converged solution required about 1 minute of computer time. The resulting liquid composition profiles for both towers are shown in figure A4.3. An interesting result shown in this figure is that the octane product may be obtained with either hexane or decane impurities by using a suitable choice of side streams locations. For instance, some runs with different locations of the octane product side stream were performed. A

low location of the side stream resulted in increased amount of decane impurity and vice versa for higher location.

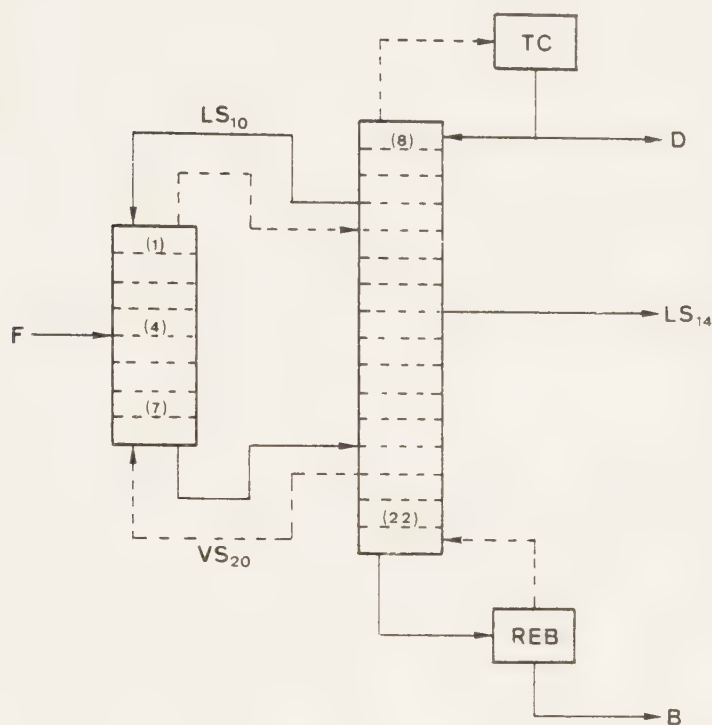


Figure 8. Petlyuk towers.

7.4 Example 4

This is the same as example 5.3 in Holland's book⁵ and is related to the distillation of wide-boiling mixtures. An 11 component hydrocarbon mixture is distilled in a single tower with 11 ideal plates. The distillation is performed at a pressure of 1825 kPa. The equilibrium and enthalpy correlations in Holland's book are used after a slight modification of the equilibrium data because of a print error in the book. These correlations are reproduced in tables A3.5 and A3.6. According to vapor-liquid equilibrium data, the boiling point is about -110°C for the lightest component, CH_4 , and about 336°C for the heaviest component, which is a so called 360°F normal boiling fraction. A saturated liquid feed of flow rate 100.0 kmol/h and composition according to table A3.7 is introduced on the fourth plate of the tower. A reboiler with the product rate set to 68.4 kmol/h and a partial condenser with a reflux ratio of 2.0 are also used.

All attempts to simulate the system specified above with the method de-

scribed in § 4 failed to converge. The method used for flow rate calculations gives erratic flow rates for wide-boiling mixtures. This difficulty is very well outlined by Friday¹⁸ who also suggests 'the use of the so-called "sum-rates" (SR) method for problems involving wide-boiling mixtures. The incorporation of the SR method in DESTLA is described in appendix 5. With this incorporation a converged solution was obtained within a CPU-time consumption of about 40 seconds. The resulting component flow rates for the product streams are shown in table A3.7 while the vapor flow rate and temperature profiles are given in table A3.8. The result deviates slightly from that obtained by Holland⁵ which is most probably due to the difference in the thermodynamic data.

This example was also solved using the assumption of constant molar flow rates. Convergence was achieved with the original solution method using about 17 seconds of CPU-time. The result from this simulation is also given in tables A3.7 and A3.8. A comparison with the solution using the SR method indicates that the assumption of constant molar flow rates gives approximately correct product compositions and a slightly erroneous temperature profile while, naturally, the vapor and liquid flow rates in the tower are completely erroneous.

7.5 Conclusions

The main objective of these examples is to demonstrate the degree of flexibility of DESTLA. Other test examples were run both for educational and research purposes. One example is the separation of acetone and methanol which form an azeotrope, by extractive distillation using water^{38,44}. Another example is the separation of an azeotropic system exhibiting partial liquid miscibility⁴⁸⁻⁵⁰, where three alternative distillation schemes for the treatment of sulfite pulping condensates were investigated. During these simulations, where interacting tower configurations are involved, almost all the equipment available in the unit cell was used.

From all test examples computed by DESTLA, it can be concluded that this computer program:

- is stable for convergence independent of the number of feeds and side-cut streams,

- allows for flexibility and ease of use both in defining and solving problems with single and multiple distillation tower configurations,
- can be effectively applied to both ideal and non-ideal systems,
- gives an approximate solution rather quickly while the final solution requires a somewhat longer computing time.

The last conclusion is especially true of non-ideal systems and configurations with a great number of plates. In the former case, about 35-40 % of the total computation time is used for vapor-liquid equilibrium calculations, while the corresponding value for ideal systems is about 20-25 %. Thus, a first attempt to reduce computation time would be to avoid the calculation of new equilibrium constants for each iteration, which is the case at present. Especially during the last iterations, the changes in the equilibrium constants are very small. This reduction in time consumption is counterbalanced by increasing core storage, as all equilibrium constants then have to be stored.

Furthermore, the same convergence acceleration routine used for the temperature calculations as described in § 4.1 could be used for the computation of the liquid compositions. This would naturally require an even larger storage space, as the relaxation factor and concentration from two previous iterations for each component and all stages have to be stored.

ACKNOWLEDGEMENTS

The author is greatly indebted to Professor Åke Jernqvist for his encouraging support and invaluable help during the course of this work. I express my sincere gratitude to Acting Professor Gharib Aly for his constructive criticism. I also wish to thank the Swedish National Board for Technical Development which partly financed this work.

LIST OF SYMBOLS

a_1, a_2, a_3, a_4	constants in equation 30	
A	heat transfer area	$ m^2 $
A_i, B_i, C_i	constants in Antoine's equation	
b_1, b_2, b_3, b_4	constants in equation 33	
b_i	bottom product flow rate of component i	$ kmole/h $
c	number of components	
C_p	heat capacity of liquid	$ kJ/kmole ^\circ C $
C_{pg}	heat capacity of vapor	$ kJ/kmole ^\circ C $
d_i	distillate flow rate of component i	$ kmole/h $
E_i	Murphree plate efficiency of component i	
f_i^{OL}	fugacity of pure liquid i	$ kPa $
F	feed flow rate	$ kmole/s $
F_I	flow rate of heating/cooling stream	$ kmole/s $
h	liquid enthalpy of a mixture	$ kJ/kmole $
H	vapor enthalpy of a mixture	$ kJ/kmole $
HF	enthalpy of feed stream	$ kJ/kmole $
H_{IN}	enthalpy of entering heating/cooling stream	$ kJ/kmole $
H_{OUT}	enthalpy of leaving heating/cooling stream	$ kJ/kmole $
ΔH_V	latent heat of vaporization	$ kJ/kmole $
K	overall heat transfer coefficient	$ kW/m^2 K $
K_i	equilibrium ratio of component i	
L	liquid flow rate	$ kmole/s $
LS	flow rate of liquid side stream	$ kmole/s $
n	iteration number	
N	number of plates or pieces of equipment	
P	pressure	$ kPa $
P_i^O	vapor pressure of component i	$ kPa $
q	pure component area parameter	

Q	heat input	[kW]
Q_L	heat losses	[kW]
r	pure component volume parameter	
R	gas law constant	[cal/g mole/K]
R	relaxation factor	
t	temperature	[°C]
T	temperature	[K]
ΔT_{LM}	logarithmic mean temperature difference	
u_{ij}	UNIQUAC binary interaction parameter	[cal/gmole]
V	vapor flow rate	[kmole/s]
V_S	flow rate of vapor side stream	[kmole/s]
x_i	liquid mole fraction of component i	
y_i	vapor mole fraction of component i	
z	lattice coordination number	
z_i	mole fraction of component i in the feed	

Greek Letters

α	relative volatility
γ_i	liquid activity coefficient of component i
$\varepsilon_1, \varepsilon_2, \varepsilon_3$	tolerance errors for convergence criteria
τ_{ij}	parameter defined in equation 26
Θ_i	area fraction of component i
Λ_{ij}	parameters in Wilson's equation
ϕ_i	fugacity coefficient for component i in the vapor phase
Φ_i	volume fraction of component i

Subscripts

d	dew point
i, j, k	typical component

j	a general plate or other unit
l	liquid
N	bottom plate in a distillation column
v	vapor
O	top plate in a distillation column

Superscripts

C	combinatorial
L	light phase
H	heavy phase
o	pure component
R	residual
s	saturated

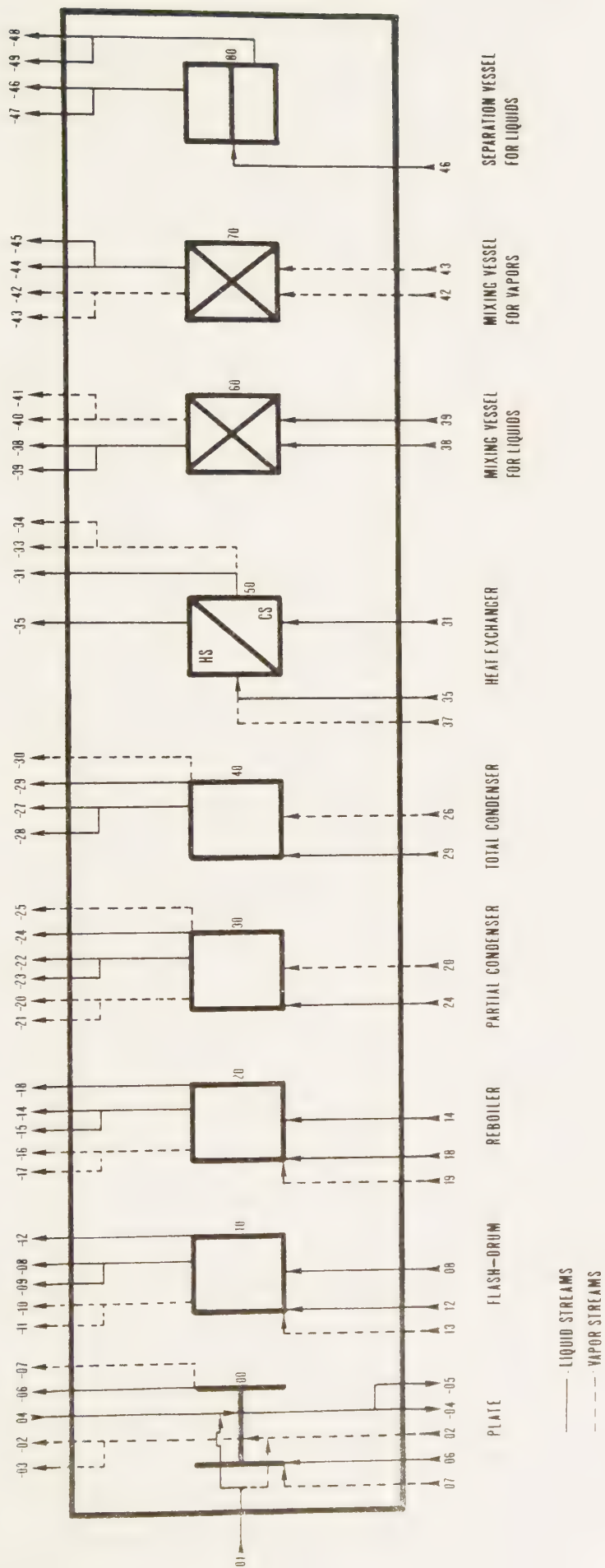
REFERENCES

1. Lewis, W.K. and Matheson, G.L. Ind. Eng. Chem. 1932, 24, 494
2. Sorel, E. "La rectification de l'alcool", Paris (1893)
3. Bonner, J.S. Chem. Eng. Progr. Symp. Ser. 1959, 55 (21), 87
4. Smith, B.D. "Design of equilibrium stage processes", McGraw-Hill, New York (1963)
5. Holland, C.D. "Multicomponent distillation", Prentice-Hall, Englewood Cliffs N.J. (1963)
6. Thiele, E.W. and Geddes, R.L. Ind. Eng. Chem. 1933, 25, 289
7. Lyster, W.N., Sullivan, S.L., Billingsley, D.S. and Holland, C.D. Petrol. Refiner 1959, 38(6), 221/1959, 38(7), 156/1959, 38(10), 139
8. Billingsley, D.S. A.I.Ch.E.J. 1970, 16, 441
9. Billingsley, D.S. Can. J. Chem. Eng. 1971, 49, 672
10. Holland, C.D. and Pendon, G.P. Hydrocarbon proc. 1974 (july), 148
11. Holland, C.D., Pendon, G.P. and Gallun, S.E. Hydrocarbon proc. 1975 (Jan), 101
12. Amundson, N.R. and Pontinen, A.J. Ind. Eng. Chem. 1958, 50, 730
13. Amundson, N.R., Pontinen, A.J. and Tierny, J.W. A.I.Ch.E.J. 1959, 5, 295
14. Wang, J.C. and Henke, G.E. Hydrocarbon Proc. 1966, 45(8), 155
15. King, C.J. "Separation processes", McGraw-Hill, New York (1971)
16. Boston, J.F. and Sullivan, S.L. Can. J. Chem. Eng. 1974, 52, 52
17. Sargent, R.W.H. and Murtagh, B.A. Trans. Instn. Chem. Eng. 1969, 47, 85
18. Friday, J.R. and Smith, B.D. A.I.Ch.E.J. 1964, 10, 698
19. Tomich, J.F. A.I.Ch.E.J. 1970, 16, 229
20. Hutchison, H.P. and Shewchuk, C.F. Trans. Instn. Chem. Engrs. 1974, 52, 325

21. Bending, M.J. and Hutchison, H.P. Chem. Eng. Sci. 1973, 62, 81
22. Goldstein, R.P. and Stanfield, R.B. Ind. Eng. Chem. Proc. Des. Dev. 1970, 9, 78
23. Naphtali, L.M. and Sandholm, D.P. A.I.Ch.E.J. 1971, 17, 148
24. Ishii, Y. and Otto, F.D. Can. J. Chem. Eng. 1973, 51, 601
25. Harclerode, H. and Gentry, J.W. Can. J. Chem. Eng. 1972, 50, 253
26. Gentry, J.W. Ind. Eng. Chem. Fund. 1970, 9, 671
27. Rose, A., Sweeny, R.F. and Schrodtt, V.N. Ind. Eng. Chem. 1958, 50, 737
28. Ishikawa, T. and Hirata, M. Bull. Jap. Petr. Inst. 1972, 14, 18
29. Jelinek, J., Hlavacek, V. and Kubicek, M. Chem. Eng. Sci. 1973, 28, 1825
30. Jelinek, J., Hlavacek, V. and Krivsky, Z. Chem. Eng. Sci. 1973, 28, 1833
31. Noh, J.C. and Lee, E.S. A.I.Ch.E.J. 1971, 17, 886
32. Lee, E.S. and Lee, P. J. Mathem. Anal. Appl. 1976, 54, 563-601
33. Jelinek, J., Hlavacek, V. and Kubicek, M. Chem. Eng. Sci. 1973, 28, 1555
34. Ricker, N.L. and Grens, A.E. A.I.Ch.E.J. 1974, 20, 238
35. Harris, R.E. Chem. Eng. Progr. 1972, 68(10), 56
36. Winter, P. and Matthew, I. Processing 1976 (July), 11
37. Jernqvist, Å. "ADJUST - an adaptive convergence algorithm for general trial and error computations", Dept. of Chem. Eng., Lund Institute of Technology, Report no. 75-F-1 (1975)
38. Zacchi, G. "DESTLA - user's manual", Dept. of Chem. Eng., Lund Institute of Technology, LUTKDH/(TKKA-3001)/1-30/(1978)
39. Gentry, J.M. Can. J. Chem. Eng. 1970, 48, 451
40. Boublik, T., Fried, V. and Hála, E. "The vapour pressures of pure substances", Elsevier, New York (1975)
41. Wilson, G.M. J. Am. Chem. Soc. 1964, 86, 127

42. Abrams, D.S. and Prausnitz, J.M. A.I.Ch.E.J. (1975), 21, 116
43. Gmeling, J. and Onken, U. "Vapor-liquid equilibrium data, collection", DECHEMA Chem. Eng. Data Series (1977)
44. Zacchi, G., Aly, G. and Jernqvist, Å. Svensk Papperstidning (1977), 80(5), 145
45. Fredenslund, A., Jones, L.R. and Prausnitz, J.M. A.I.Ch.E.J. 1975, 21, 1086
46. Olsson, B. and Svensson, S.G. "Formalindistillation II: Vapor-liquid equilibrium data for the formaldehyd-water system" Dept. of Chem. Eng., Lund Institute of Technology (1972) (in Swedish)
47. Hála, E., Wichterle, I., Polák, J. and Boublik, T. "Vapor-liquid equilibrium data at normal pressures", Pergamon Press, Oxford (1968)
48. Zacchi, G. and Aly, G. "Simulation and design of distillation units for treatment of sulfite pulping condensates to recover methanol and furfural Part I: Incorporation with an evaporation unit and use of secondary steam", Accepted for publication in the Can. J. Chem. Eng.
49. Aly, G. and Zacchi, G. "Simulation and design of distillation units for treatment of sulfite pulping condensates to recover methanol and furfural Part II: Applicability of multiple-effect distillation using live steam", Accepted for publication in the Can. J. Chem. Eng.
50. Zacchi, G. and Aly, G. "Applicability of some energy-saving techniques in a distillation process for treatment of sulfite pulping condensates and economic by-product recovery", to be presented at the third international symposium on distillation (1979)

APPENDIX 1: Unit cell



The unit cell of DESTLA.

APPENDIX 2: Typical output list from DESTLA

DATA FOR TRAYS

UNIT CELL NUMBER

3

FEED

FLOW KMOLE/H 75.000
PRESSURE KPA/SCAL 101.300
TEMPERATURE DEG C 80.000
ENTHALPY KJ/MOLE 6.036
CONC COMP 3 MOLE % .10000+03

LEAVING VAPOUR

MAIN STREAM FMOLE/H 177.939
PRE DRIE FPA/SCAL 101.300
TEMPERATURE DEG C 59.975
ENTHALPY KJ/MOLE 39.255
CONC COMP 1 MOLE % .81903+02
CONC COMP 2 MOLE % .22446+01
CONC COMP 3 MOLE % .15853+02

LEAVING LIQUID

MAIN STREAM FMOLE/H 200.417
PRESSURE KPA/SCAL 101.300
TEMPERATURE DEG C 59.975
ENTHALPY KJ/MOLE 6.065
CONC COMP 1 MOLE % .48508+02
CONC COMP 2 MOLE % .21330+01
CONC COMP 3 MOLE % .49359+02

PLATE EFFICIENCY % 90.000

DATA FOR REFLIERS

UNIT CELL NUMBER

20

LEAVING VAPOUR

MAIN STREAM KMOLE/H 161.303
PRESSURE KPA/SCAL 101.300
TEMPERATURE DEG C 71.080
ENTHALPY KJ/MOLE 41.756
CONC COMP 1 MOLE % .19513+02
CONC COMP 2 MOLE % .58747+02
CONC COMP 3 MOLE % .21740+02

LEAVING LIQUID

MAIN STREAM KMOLE/H 124.999
PRESSURE KPA/SCAL 101.300
TEMPERATURE DEG C 71.080
ENTHALPY KJ/MOLE 5.647
CONC COMP 1 MOLE % .39374+01
CONC COMP 2 MOLE % .39047+02
CONC COMP 3 MOLE % .57016+02

HEATING STREAM - IN

FLOW KMOLE/H 150.000
PRESSURE KPA/SCAL 300.000
TEMPERATURE DEG C 133.500
ENTHALPY KJ/MOLE 49.060
CONC COMP 3 MOLE % .10000+03

HEATING STREAM - OUT

TEMPERATURE DEG C 133.510
ENTHALPY KJ/MOLE 10.073

HEAT TRANSFER KW 1631.811

DATA FOR TOTAL CONDENSERS

UNIT CELL NUMBER

1

LEAVING LIQUID

MAIN STREAM KMOLE/H 129.450
SIDE STREAM FMOLE/H 50.000
PRESSURE KPA/SCAL 101.300
TEMPERATURE DEG C 46.371
ENTHALPY KJ/MOLE 5.707
CONC COMP 1 MOLE % .90141+02
CONC COMP 2 MOLE % .23906+01
CONC COMP 3 MOLE % .74679+01

SUBCOOLING DEG C 10.000

Typical output list from DESTLA (taken from ref. 38).

APPENDIX 3: Tables for the computed examples

Table A3.1 Antoine's constants for the components of example 1.

Component i	A_i	B_i	C_i
phenol (1)	7.13301	1516.79	174.954
o-cresol (2)	6.91172	1435.503	165.158
p-cresol (3)	7.03508	1511.08	161.854
m-cresol (4)	7.50798	1856.356	199.065

Table A3.2 Activity coefficients at infinite dilution and azeotropic data for the binaries of example 2.

System	γ_1^∞	γ_2^∞	Azeotropic data	
			x_1 (mole %)	T ($^{\circ}\text{C}$)
Methanol (1) - Isopropanol (2)	1.23	1.27	-	-
Methanol (1) - Toluene (2)	11.27	15.22	85.9	62.2
Isopropanol (1) - Toluene (2)	3.98	3.30	86.7	81.7

Table A3.3 Antoine's and Wilson's constants for the methanol-isopropanol-toluene system

<u>Antoine's constants</u>			
Component i	A_i	B_i	C_i
Methanol (1)	8.07246	1574.990	238.86
Isopropanol (2)	7.75634	1366.142	197.97
Toluene (3)	6.95334	1343.943	219.377

<u>Wilson's constants (Λ_{ij})</u>			
Comp i \ Comp j	Methanol	Isopropanol	Toluene
Methanol	1.0	1.0267	0.2087
Isopropanol	0.7683	1.0	0.3922
Toluene	0.1450	0.5558	1.0

Table A3.4 Antoine's constants for hexane, octane and decane

Component i	A_i	B_i	C_i
Hexane	6.88555	1175.817	224.867
Octane	6.91874	1351.756	209.100
Decane	6.95707	1503.568	194.738

Table A3.5 Equilibrium constants for the components of example 4

Component	a_1	a_2	a_3
CH ₄	63.76528	-29.51969	4.25794
C ₂ H ₆	10.93719	-3.88431	0.55580
C ₃ H ₆	4.03335	-1.14742	0.17389
C ₃ H ₈	3.64797	-1.06605	0.16197
i-C ₄	1.46077	-0.18097	0.02721
n-C ₄	1.00000	0.00000	0.00000
n-C ₅	0.17185	0.22019	-0.02826
n-C ₆	0.00541	0.14775	-0.01056
n-C ₇	-0.02141	0.07538	0.00061
n-C ₈	-0.01184	0.02524	0.00593
360	-0.00145	-0.00053	0.00430

$$K^* \text{ (for n-C}_4\text{)} = 0.193 - 0.117 (T/100) + 0.229 (T/100)^2 - 0.011 (T/100)^3$$

$$K_i = K^* [a_{1i} + a_{2i} (T/100) + a_{3i} (T/100)^2]$$

(T in °F)

Table A3.6 Enthalpy data for the components of example 4

Component	b_1	b_2	b_3	c_1	c_2	c_3
CH ₄	1840.25	1345.33	-11.110	4864.17	773.26	19.0294
C ₂ H ₆	3147.12	2222.47	10.935	8384.48	1280.67	65.9954
C ₃ H ₆	4213.82	2874.12	40.076	11254.87	1746.81	102.5564
C ₃ H ₈	4425.16	2968.64	48.868	11806.71	1797.38	112.6239
i-C ₄	5320.76	3525.03	90.076	13726.02	2261.20	167.3186
n-C ₄	5553.24	3641.27	90.076	14851.06	2312.00	155.9965
n-C ₅	6663.21	4161.81	160.848	18757.52	2903.45	233.0578
n-C ₆	7661.12	4658.30	231.661	20445.36	3207.59	287.9913
n-C ₇	8676.69	5066.88	310.574	23038.41	3713.28	328.7941
n-C ₈	9845.04	5353.77	403.497	25539.97	4119.20	405.9716
360	11509.74	6023.85	599.071	30246.89	5121.06	524.2676

$$h_i = b_{1i} + b_{2i} (T/100) + b_{3i} (T/100)^2; \quad h = \sum_{i=1}^C h_i \cdot x_i$$

$$H_i = c_{1i} + c_{2i} (T/100) + c_{3i} (T/100)^2; \quad H = \sum_{i=1}^C H_i \cdot y_i$$

(T in °F)

Table A3.7 Component flow rates, in kmol/h, for feed, distillate, and bottom streams of example 4

Component i	f_i	d_i	b_i	d_i^*	b_i^*
CH ₄	2.0	2.0000	-	2.0000	-
C ₂ H ₆	10.0	10.0004	-	10.0005	-
C ₃ H ₆	6.0	5.9650	0.0365	5.9544	0.0488
C ₃ H ₈	12.5	12.2646	0.2388	12.1941	0.3145
i-C ₄	3.5	0.6610	2.8382	0.6653	2.8337
n-C ₄	15.0	0.6992	14.2963	0.7785	14.2149
n-C ₅	15.2	0.0059	15.1916	0.0074	15.1896
n-C ₆	11.3	0.0001	11.2990	0.0001	11.2990
n-C ₇	9.0	-	9.0001	-	9.0001
n-C ₈	8.5	-	8.5001	-	8.5001
360	7.0	-	7.0000	-	7.0000

* solution obtained with assumption of constant molar flow rates.
flow rates < 0.0001 kmol/h are omitted

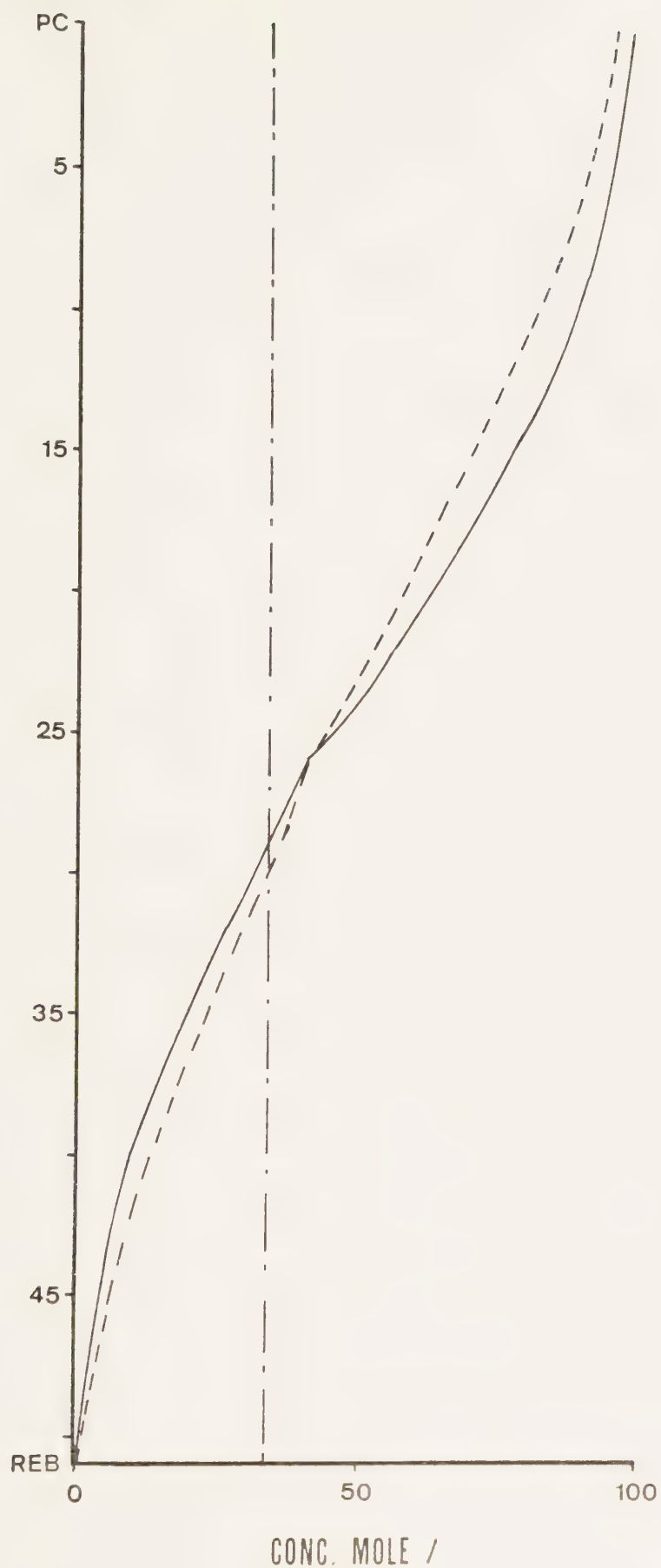
Table A3.8 Vapor flow rate and temperature profiles of example 4

Plate j	V_j (kmole/h)	T_j ($^{\circ}\text{C}$)	V_j^* (kmole/h)	T_j^* ($^{\circ}\text{C}$)
P. c.	31.60	35.61	31.60	36.06
1	94.79	51.00	94.80	51.81
2	94.05	61.01	94.80	62.31
3	90.26	71.75	94.80	74.24
4	81.06	91.75	94.80	97.81
5	107.38	103.04	94.80	109.34
6	119.05	110.83	94.80	116.67
7	126.13	116.93	94.80	122.23
8	131.01	122.06	94.80	126.82
9	133.80	127.04	94.80	131.09
10	133.89	133.30	94.80	136.22
11	129.68	143.99	94.80	145.13
Reb.	116.26	168.00	94.80	167.79

*solution obtained with assumption of constant molar flow rates

APPENDIX 4: Figures for the computed examples

PLATE NO



-----initial
-----intermediate (50 % of total number of iterations)
-----final

Figure A4.1 Liquid-phase concentration profile for phenol.

PLATE NO

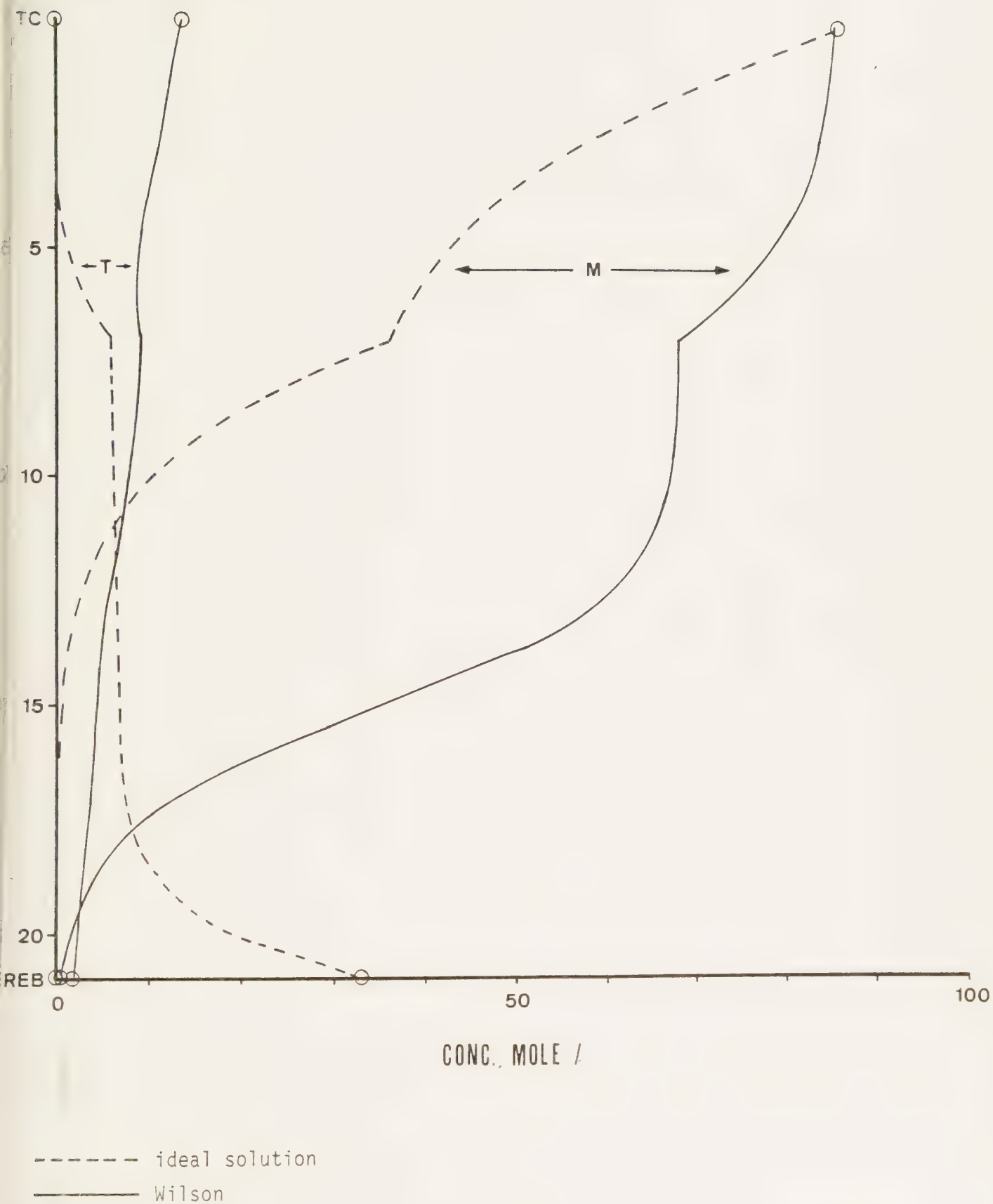


Figure A4.2 Liquid-phase concentration profiles for methanol(M) and toluene(T).

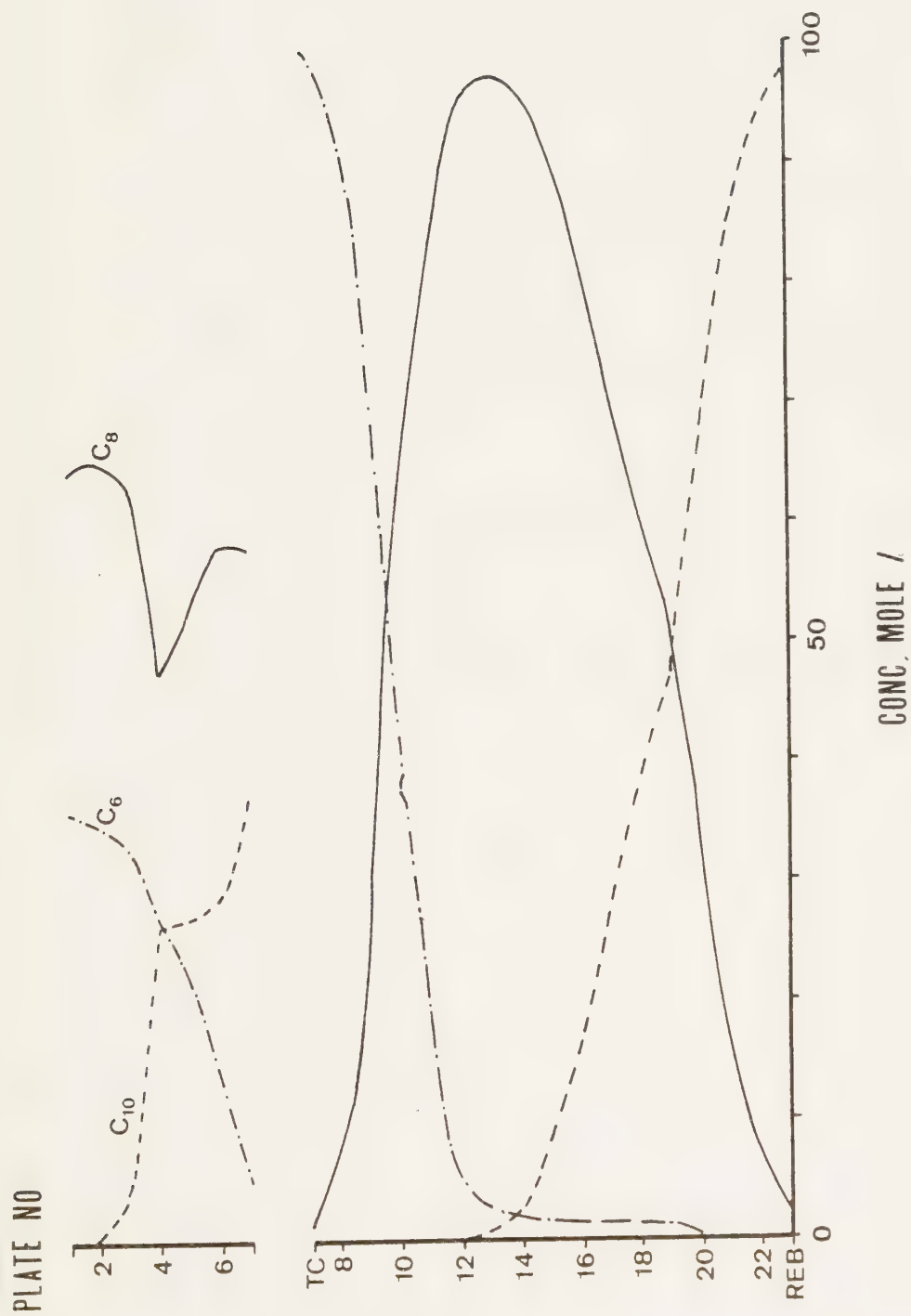


Figure A4.3 Liquid-phase concentration profiles for the Petlyuk towers.

Modified solution method for systems of wide-boiling components

The solution method described in § 4.1 has proved to be numerically unstable when applied to mixtures of wide-boiling components. The main reason is the numerical procedure utilized in flow rate computation which, for wide-boiling components may give erratic flow rates. This can be explained by examining the following equation:

$$(L_j + LS_j) = \frac{F_j(HF_j - H_j) + L_{j-1}(h_{j-1} - H_j) + V_{j+1}(H_{j+1} - H_j) + Q_j - QL_j}{(h_j - H_j)} \quad (A1)$$

The denominator may become positive during the iterative calculations and thus give indeterminate flow rates. In order to overcome this inconvenience the sum-rates method is adopted in DESTLA.

The computational procedure is principally the same as described in § 4.1 with the modifications outlined below.

Step_1: Computation of component flow rates using the same equations as for step 2 in § 4.1. A L_j/V_j ratio obtained from a previous iteration is used (see step 4).

Step_2: The liquid and vapor flow rates are calculated using a modification of the summation equation

$$\sum_{i=1}^C v_{i,j} = V_j \quad ; \quad \sum_{i=1}^C l_{i,j} = L_j \quad (A2)$$

where $v_{i,j} = y_{i,j} \cdot V_j$ and $l_{i,j} = x_{i,j} \cdot L_j$ are obtained from step 1 above.

Step_3: A new temperature is assumed using a similar procedure as in § 4.1.

The summation equation term $(\sum_{i=1}^C x_{i,j} - 1.0)$ in equation (14) is replaced by a term, ΔQ , determining the imbalance in the enthalpy balance equation. ΔQ is defined according to the following equations:

$$\Delta Q = (Q_{IN} - Q_{OUT})/Q_{IN} \quad (A3)$$

where

$$Q_{IN} = F_j HF_j + L_{j-1} h_{j-1} + V_{j+1} H_{j+1} + Q_j \quad (A4)$$

and

$$Q_{OUT} = (V_j + VS_j)H_j + (L_j + LS_j)h_j + QL_j \quad (A5)$$

Step 4: A new L_j/V_j ratio is calculated if $|\Delta Q| < \epsilon_3$, otherwise the previous L_j/V_j ratio is retained. The tolerance error ϵ_3 is at present set to 0.01.

When the above solution method is used, the convergence criteria described in § 4.2 are modified. The bubble-point check is replaced by a check on ΔQ , using the same tolerance error ϵ_1 , while the test based on the component mass balance around the distillation column is retained. Furthermore, a third criteria for the L_j/V_j ratio is introduced, where a maximum difference of 0.1 % in the ratios obtained in two consecutive iterations is allowed.

The selection of solution method in DESTLA is based on the enthalpy data for the system under consideration. Vapor and liquid enthalpies for the pure components involved are evaluated at a mean value of pressure and temperature. In cases where the maximum value of liquid enthalpy is greater than the minimum value of vapor enthalpy, i.e.

$$(h_i^O)_{\max} > (H_i^O)_{\min} \quad (A6)$$

the above solution method is used. In all other cases the solution method described in § 4.1 is applied.

SIMULATION AND DESIGN OF DISTILLATION
UNITS FOR TREATMENT OF SULFITE PULPING
CONDENSATES TO RECOVER METHANOL AND
FURFURAL

PART I: INCORPORATION WITH AN EVAPOR-
ATION UNIT AND USE OF SECONDARY
STEAM

GUIDO ZACCHI AND GHARIB ALY

DEPARTMENT OF CHEMICAL ENGINEERING
LUND INSTITUTE OF TECHNOLOGY
LUND
SWEDEN

SUMMARY

A distillation unit was simulated using DESTLA, a computer program for steady-state calculations of general multicomponent distillation units. Vapor-liquid and liquid-liquid equilibria were both computed by EQUIL, a computer program for computation and plotting of such equilibria. The simulations resulted in a distillation unit consisting of three columns. Energy consumed in the first column dominates the operating costs of the unit. The first of the three different alternatives studied for satisfying the energy requirements of the first column is presented. Incorporating the first column into an evaporation unit yields low steam consumption. However, a decrease in evaporation capacity due to the temperature drop in the first column and complex control design are the disadvantages associated with this alternative.

INTRODUCTION

The condensate effluent from bisulfite pulping contains, among other organic substances, methanol and furfural. These contribute to environmental problem and have significant economic value as well if they can be recovered. It seemed that distillation might offer a potential method for solving this problem. Since computer programs for dealing with complicated problems of this type were available, an investigation was undertaken to examine the feasibility of such a process.

The cooking condensate and the spent sulfite liquor in the magnesite process at Nymölla contain chemical byproducts from the pulping of wood, including sulfur dioxide, methanol, acetone, acetaldehyde, furfural, p-cymene and acetic acid. The type and amount of each chemical in any given batch depend on the wood species, the cooking liquor and the cooking operating conditions.

The spent sulfite pulping liquor is treated conventionally by evaporation and subsequent burning to produce steam and power and to recover the chemicals for reuse in the cooking operation. During evaporation, some of the above mentioned chemical products are vaporised. The type and amount of organic chemicals evolved - mainly methanol, furfural and acetic acid - depend mainly on the temperature level maintained in each effect and the pH value of the liquor.

In disposing of both the various condensed gases released during the cooking operation and the condensate streams from the evaporation plant there are economic and environmental factors to be considered. Much effort has been expended in recent years in order to find an economical and practical means of disposing these condensates. However, no commercially acceptable process for recovering these chemicals has been developed. Most of the prior art processes recover only one chemical from a given effluent stream. As well, the purity of the organic chemicals recovered by previously known processes is poor, further processing being often required to obtain saleable products.

Baierl¹ described a method of recovering methanol and furfural from a sulfite pulp effluent by treating the effluent with steam in a fractionating column. The quality of the recovered chemicals was improved by a preliminary steam stripping prior to fractionation, thus removing

the bulk of SO_2 content. The furfural fraction was about 90 % pure while the methanol fraction about 93 % pure. The live steam consumption varied between 10-12 % of the feed. According to Hough and Sallee², steam stripping of sulfate pulping condensates requires a steam rate of 15-18 % by weight of the feed rate.

Many authors have suggested that furfural can be extracted directly from the condensate by means of trichloroethylene^{3,4}, toluene⁵, or poly halogenated benzenes⁶. Adsorption on active carbon, alumina or silica gel was also suggested for furfural recovery^{7,8}. However, a recently published investigation⁹ concluded that a recovery system for furfural and acetic acid based on adsorption and distillation is uneconomic. This investigation envisaged that the evaporation condensate was first steam-stripped and then treated in two adsorption towers packed with active carbon. Furfural was desorbed by methanol vapor and the mixture distilled to give 86 % furfural; acetic acid was desorbed by steam and the solution distilled to give 93 weight % acetic acid.

The purpose of the present work was to investigate the potential of using distillation to treat sulfite pulping condensates, from both cooking and evaporation units, for the recovery of economic byproducts, essentially methanol and furfural. Rather than examining just the distillation process as such, the primary emphasis has been focused on economising the energy needs for a unit operation of this type, since the operating cost plays an important role in determining the profitability of the entire process. For this purpose three possible alternatives, the first of which is presented in this paper, have been investigated during the course of the present work. As means for simulating these alternatives, DESTLA, a computer program for calculation of general multicomponent distillation systems¹⁰, has proved to be a very useful tool. The data used in these simulations represents the actual situation in the Nymölla plant. This data is tabulated in Table 1. About 70 % of the total amount of methanol and furfural in a sulfite pulping process is present in the condensate stream leaving evaporation effects 4 and 5¹¹. The cooking condensate contains about 15 % and the balance is usually found in the condensate leaving the condenser system in the evaporation unit.

TABLE 1: BASE DATA FOR THE CONDENSATE STREAMS

	Cooking condensate	Evaporation condensate	Total
Flow rate, kg/s	2.5	17.8	20.3
Conc. of methanol, kg/m ³	-	-	2.1
Conc. of furfural, kg/m ³	2.5	1.5	1.6

EQUILIBRIUM DATA

Experimental equilibrium data are available for the binary systems of methanol-water¹², methanol-furfural¹³, and water-furfural¹⁴. The Antoine constants and the physical properties of the pure components can be found in text books^{12,15}.

The Wilson parameters used to calculate the activity coefficients for the methanol-water-furfural system were computed by the computer program EQUIL¹⁶. The computed values are given in Table 2. For the water-furfural binary, Wilson parameters together with Antoine constants were used in the same computer program to simulate and plot equilibrium information. The equilibrium curve obtained is shown as the dotted line in Figure 1. Since this binary has a heterogeneous azeotrope and since Wilson's equation has the undesirable feature of its inapplicability to liquid mixtures with only partial miscibility, the recently developed UNIQUAC equation¹⁷ was adopted in this work. The computed UNIQUAC parameters for our system are tabulated in Table 2.

TABLE 2: EQUILIBRIUM DATA FOR THE TERNARY SYSTEM

Parameter	Component i		
	Methanol	Water	Furfural
Wilson's Λ_{ij}	1.000	0.410	0.076
	1.068	1.000	0.207
	0.525	0.037	1.000
UNIQUAC's $u_{ij} - u_{jj}$	0.00	-341.08	-171.92
	538.04	0.00	943.37
	1682.10	-88.96	0.00

The equilibrium curve for the water-furfural binary was computed and plotted once again using UNIQUAC parameters instead of Wilson's. The result is shown as the full line in Figure 1. As can be seen, the immiscibility of the system was successfully detected. The experimental data points used in curve fitting are also marked in the same figure for comparison.

CALCULATION OF DISTILLATION COLUMNS

The present separation problem requires the fractionation of the methanol-water-furfural system into three nearly pure fractions. The water-furfural binary has a heterogeneous azeotrope and may be readily separated completely utilizing two columns and a suitable liquid-liquid decanter. However, using two columns to fractionate our ternary system would be uneconomic because of an unacceptable high steam consumption in the first column whereinto the feed is introduced. A third column, referred to as the primary stripper, is thus needed in which the volatile organic components are stripped by means of steam.

For our feed and product specifications, the total reboiler heat duty will dominate the operating cost; thus it is necessary to keep the energy consumption of such a distillation unit as low as possible. For this reason, three different alternatives for supplying steam to the primary stripper were studied. The first alternative would use secondary steam already available in the plant by incorporating this stripper with the evaporation unit. Live steam and application of multi-effect distillation were investigated in the other two alternatives, which will be presented in the part II of this work.

The distillation unit consisting of a primary stripper and two upgrading columns was simulated by DESTLA¹⁰, a computer program which is based on a modular general distillation plant and uses so-called unit cells together with a description of the plant flow sheet as a connection matrix. The unit cell, shown in Figure 2, is a module which enables the user to assemble flow sheets of distillation plants of arbitrary complexity. The module used here comprises a tower plate, a flasher, a reboiler, a partial condenser, a total condenser, a heat exchanger, a liquid mixing vessel, a vapor mixing vessel, and a liquid separation vessel. Flowsheet data is entered via a special connection matrix. Data concerning all incoming streams, reflux ratios or condenser duties, and reboiler duties are also required. Information on vapor-liquid equilibria can be supplied in two different ways. If the equations already available in the program are to be used, some binary parameters must be given. Alternatively, the user may supply his own subprograms specifying this information. Furthermore, for systems known to behave nonideally, detailed enthalpy data for both vapor and liquid mixtures should be given; otherwise the program will

automatically assume constant molar heats of vaporization. As output information, DESTLA delivers all important data calculated such as flow rate, composition, temperature, pressure and heat content of the streams entering or leaving each piece of equipment in the modular unit cell.

Flow sheet description

The flow sheet in Figure 3 shows the main equipment in the distillation unit. For simplicity, feed and storage tanks, heat exchangers, pumps and pipes are not shown in the figure but were considered in the economic analysis. The feed F is preheated and pumped to column I, the primary stripper, which utilizes secondary steam S1 from the first effect E1 of the evaporation unit. The pressure in this column is about 200 kPa. The stripped condensate is taken out as bottoms B1 while the overhead stream is condensed in the second effect E2. The stream D1 is partially cooled before being pumped to column II via a storage tank. The overhead product D2, which is nearly pure methanol, is cooled before being pumped to the methanol storage tank. Nearly pure condensate is taken out as bottoms B2 while a liquid side stream SS, containing the highest furfural concentration in this column, is withdrawn and sent to the liquid separation vessel SEP after being subcooled to 30°C. This two-phase mixture is separated into two liquid layers. The water-rich layer AQ is preheated and refluxed to the column while the furfural-rich layer ORG is preheated and pumped to column III, via a storage tank.

Column II, referred to as the methanol column, operates at atmospheric pressure and utilizes live steam S2 available in the plant at 0.4 MPa. Column III, referred to as the furfural column, operates at 50 kPa and utilizes live steam S3 at 1.0 MPa as the energy source in its reboiler. Nearly pure furfural is taken out as bottoms B3, subcooled and pumped to the furfural storage tank. The overhead V3 is condensed and subcooled in TC2 to 30°C before entering the liquid separation vessel SEP.

Assumptions and environmental requirements

The simulations were based on the following assumptions:

1. The condensate is treated as a ternary system consisting of methanol, water and furfural. Only the condensates from the cooking unit and

effects 4 and 5 in both evaporation lines of the Nymölla process will be treated.

2. At least 90 % of the furfural and of methanol will be recovered.
3. The furfural product contains less than 0.1 weight % of methanol and water. The purity of the methanol product should be at least 97 weight %.
4. The primary stripper is incorporated between two evaporation effects in the second evaporation line of the Nymölla process. The secondary steam from the first effect E1 has a pressure of 203 kPa and amounts to 8 kg/s. Its content of volatile components is neglected.
5. The total temperature drop in the primary stripper should not exceed 6-7°C.

Computation procedure

The primary stripper was simulated separately while the methanol and furfural columns were linked together and simulated as one unit since both columns have one liquid separation vessel in common. The vapor-liquid equilibria in both columns were computed using Wilson's parameters while the liquid-liquid equilibrium in the separation vessel was computed using UNIQUAC's.

In the primary stripper, the methanol concentration in the overhead stream should not exceed 3.5 weight % in order to satisfy the temperature drop requirement according to assumption 5 above. The reflux ratio is now fixed since the amount of the stripping steam is also known. The number of ideal stages as well as the optimum feed location were computed by trial and error with assumption 2 as the optimizing criterion. This assumption was satisfactorily fulfilled by using a total of 6 ideal plates with the feed entering on the second plate. All plates are numbered from the top downwards.

In the methanol column, the total number of ideal stages was fixed at 16 (15 plates plus reboiler). For a certain value of S_2 (or reflux ratio), the optimum feed and side stream locations were computed with assumptions 2 and 3 as criteria. These assumptions are fulfilled if the feed enters on the ninth plate and if the side stream SS is withdrawn from the fifth

plate. The reflux stream AQ is fed back to the sixth plate. In order to satisfy the furfural purity requirement, only 4 ideal stages are needed in the furfural column with the feed, stream ORG, being entered on the first plate.

Computation results

The results of some runs carried out by DESTLA are summarized in Table 3 and Table 4 as well as Figure 4.

TABLE 3: COMPONENT FLOW RATES, IN kg/h, FOR INPUT, OUTPUT AND ENERGY STREAMS

Component	Input Streams		Purified condensate		Byproducts		Energy Streams	
	F	S1	B1	B2	B3	D2	S2	S3
Methanol	153.3	--	3.3	0.2	≈0	149.8	--	--
Water	72730	28800	97416	4111	≈0	3.2	1864	60
Furfural	116.8	--	4.2	0.2	112.3	0.1	--	--

As far as the quality of the products is concerned, it can be observed that the methanol column produces 153 kg/h of methanol with 97.8 weight % in purity while the furfural column produces 112 kg pure furfural per hour. About 96 % of the purified condensate will be taken out at 121°C from the primary stripper while 4 % leaves the methanol column at 107°C. Before being circulated for reuse in the mill these streams are used to preheat the feed to the primary stripper. As can be seen from Table 3, the total organic content in streams B1 and B2 is about 4 kg of methanol and 5 kg of furfural per hour. This means that a considerable reduction in the COD and BOD₅ of the condensate can be achieved. The live steam consumption in the methanol and furfural columns amounts to 2.6 % by weight of the condensate stream to be treated. The temperature drop in the primary stripper is approximately 7°C as can be deduced from Table 4. This drop is partly due to the pressure drop in the column, taken as 1 kPa per plate, and partly due to the difference between bubble points at the top and bottom of the column (4°C). Heat losses from the column were neglected.

TABLE 4: SUMMARY OF RESULTS COMPUTED BY DESTLA FOR THE THREE DISTILLATION COLUMNS

	Primary stripper				Methanol column				Furfural column			
	F	S1	B1	D1	D2	B2	SS	AQ	ORG	V3	B3	
Flow rate, kg/h	73000	28800	97424	4376	153	4111	975	863	193	81	112	
Methanol conc., wt-%	0.21	--	0*	3.4	97.8	0*	7.3	8.2	1.3	3.0	0*	
Water conc., wt-%	99.63	100.0	100.0	94.0	2.1	100.0	73.5	83.1	13.3	31.8	0*	
Furfural conc., wt-%	0.16	--	0*	2.6	0.1	0*	19.2	8.7	85.4	65.2	100.0	
Temp., °C	110	121	121	117	65	100	92	90 [†]	90 [†]	102 [†]	137	
Adjusted temp., ** °C				114		107	95 [†]					

** adjusted for pressure drop in column

* these concentrations are < 0.05 wt-%

† temperature in liquid separation vessel (SEP) = 30°C

Figure 4 displays the concentration profiles computed by DESTLA for the methanol column. It can be seen that the side stream SS, withdrawn from the fifth plate, has a relatively high concentration of furfural and a low concentration of methanol. Other plate locations for the reflux stream AQ were simulated, both over and beneath the side stream plate. It was found that this location has a little influence on the furfural and methanol concentration profiles.

The CPU-time consumed by DESTLA in simulating the primary stripper was 0.5 sec on a UNIVAC-1108 computer system. In simulating both methanol and furfural columns linked together by the liquid separation vessel, DESTLA connected together 18 plates, 2 reboilers, 2 total condensers, 3 heat exchangers, one liquid mixing vessel, and a liquid separation vessel. In this case DESTLA consumed about 6 minutes. Computation of liquid-liquid equilibria was the most time consuming part in these simulations since full convergence was required in the separation vessel.

DISCUSSION

The simulations discussed above clearly indicate the potential of using distillation as a suitable method for the treatment of condensate streams to recover nearly pure furfural and methanol.

According to the assumptions used in the simulations, neither acetic acid nor SO_2 were taken into consideration. However, these components together with some others would appear in a real distillation unit. SO_2 would be vented out from the steam trap attached to the second evaporation effect E2 and can eventually be reused in the preparation of cooking liquor. As far as the acetic acid is concerned, a simulation has been carried out using DESTLA in order to compute the concentration of this component in the purified condensate streams B1 and B2. More than 97 % of the free acetic acid will be taken out in the bottom stream, B1, leaving the primary stripper while the balance will be made with B2. This simulation confirmed the results obtained by Tsirlin¹⁸ who experimentally investigated a similar distillation system.

Using secondary steam from an existing evaporation unit as the energy source in the primary stripper has the very great advantage of low steam consumption. On the other hand, incorporating the primary stripper in an evaporation line also has some disadvantages. Firstly the temperature drop of 7°C in the stripper gives rise to a drop in evaporation capacity. This drop must be compensated for correspondingly by inserting an extra heating area in the evaporation unit. In the Nymölla case, an excess area of about 700 m^2 will be required if the evaporation capacity is to be maintained at its original level. Secondly, a properly designed evaporation unit will consume less live steam if operated in a 6-effect mode compared to a 5-effect mode. In the former mode of operation, about 13 % of the live steam consumption can be saved. If it is not practically possible to operate the evaporation unit with the stripper incorporated in a 6-effect mode this saving can not be realized. The increase in live steam consumption, caused by a 5-effect mode of operation, should in fact be charged to the primary stripper. Consequently, the live steam consumption in the distillation unit would actually be 7.5 % by weight of the condensate to be treated. Lastly, the stripper being incorporated in an evaporation unit with fluctuating operating conditions necessitates a rigorous control scheme to be undertaken so as to guarantee both the

specified concentrations in the distillation unit and the washing cycle requirements of the evaporation line.

To conclude, incorporating the primary stripper into an evaporation unit seems to be promising from the view point of steam consumption. Although the complex design makes it difficult to add a stripper to an existing evaporation unit, this incorporation should be considered for a new sulfite pulp mill.

Part II of this work¹⁹ will include the results of the other two alternatives, an economic analysis, and an experimental investigation concerning the treatment of a condensate stream by batch distillation.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. Lars Aggebrandt, Mr. Torsten Svenland, and Mr. Peter Wickström of the Nymölla AB, Sweden, for initiating this investigation, for supplying the necessary stream data, and for their kind permission to publish the results.

REFERENCES

1. Baierl, K.W., US Patent 3764462 (1973).
2. Hough, G.W. and Sallee, R.W., Tappi, 60(2), 83 (1977).
3. Ruchai, N.S. et al, Hidrolii. Lesokhim. Prom. 1, 7-9 (1975).
4. Ibid, 6, 10-12 (1974).
5. Dunning, J.W., Frye, C.F. and Lathrop, E.C., US Patent 2559607 (1951).
6. Dunlop, A.P., US Patent 2536732 (1951).
7. Cass, O.W., US Patent 2779770 (1957).
8. Khol'kin et al, Khim. Tekhnol. Drev., 1, 35(41) (1973).
9. Kringstad, K., "Waste products from forest industry as raw materials for chemicals and protein", in Swedish, STU-report 75-5768 (1977).
10. Zacchi, G., "DESTLA - a computer program for calculation of general multicomponent distillation systems.", Report LUTKDH/(TKKA-3001)/1-40/(1978), Dept of Chem Eng, Lund Institute of Technology (1978).
11. Angpanneföreningen/AB Energi Konsult, "SSVL:s Development Project 3:3" in Swedish, (1973).
12. Hála, E., Wichterle, I., Polák, J. and Boublik, T., "Vapour-liquid equilibrium data at normal pressures", Pergamon Press, Oxford (1968).
13. Andreev, K.P. and Tsirlin, Y.A., Zh. Prikl Khim. 27, 402 (1954).
14. Tsirlin, Y.A., Russian Journal of Physical Chemistry, 36(8), 903 (1962).
15. Boublik, T., Fried, V. and Hála, E., "The vapour pressures of pure substances", Elsevier, Amsterdam (1973).
16. Zacchi, G., Aly, G. and Jernqvist, Å., Swedish Paper Journal, 80(5), 145 (1977).
17. Abrams, D.S. and Prausnitz, J.M., AIChE Journal 21, 116 (1975).
18. Tsirlin, Y.A., Zh. Prikl. Khim., 35(2), 409 (1962).
19. Aly, G. and Zacchi, G., Can. J. Chem. Eng., submitted for publication.

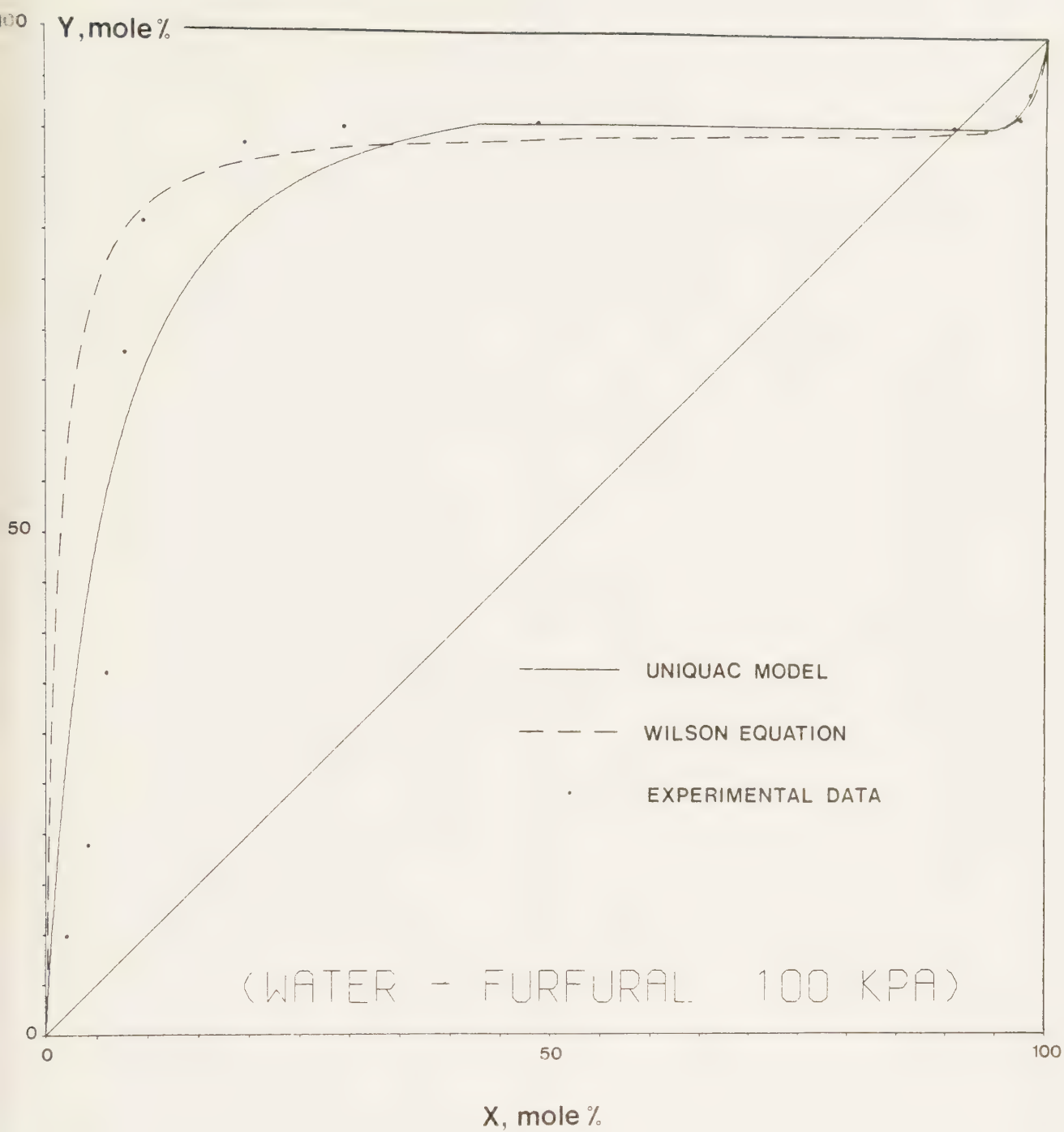


Figure 1. Equilibrium curve for the water-furfural system at 100 kPa.

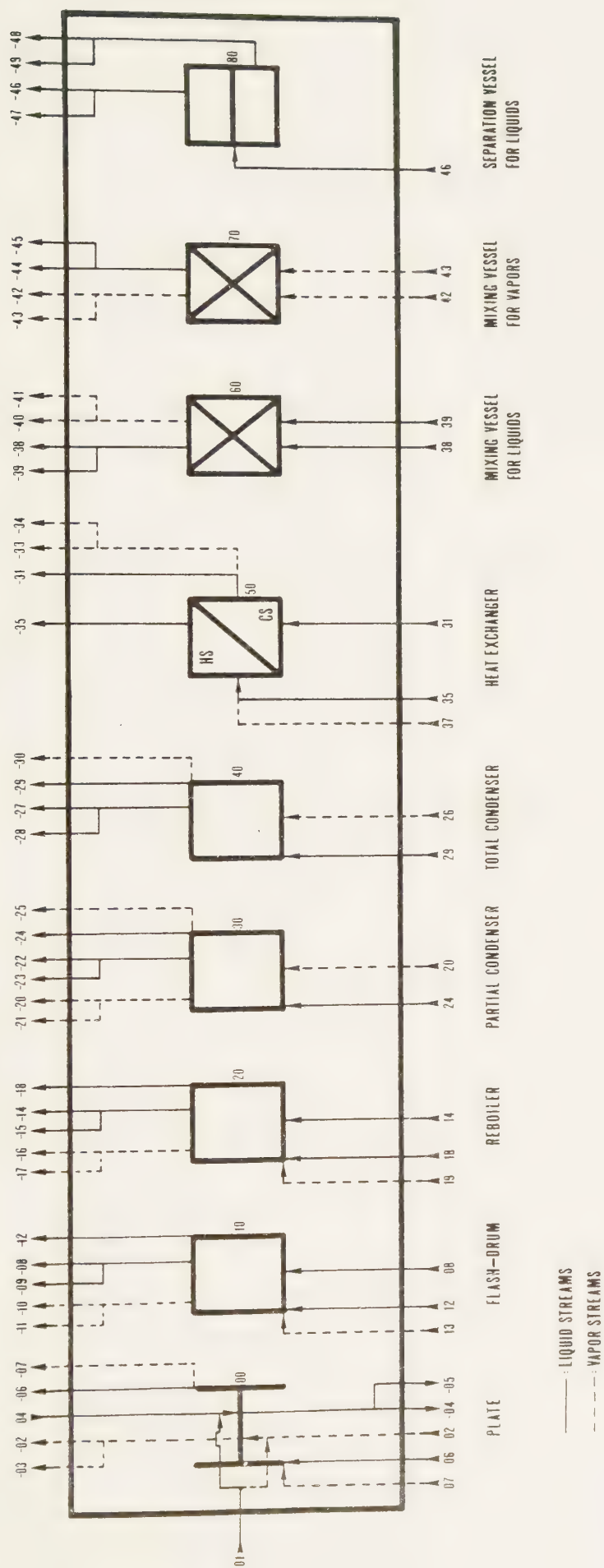


Figure 2. DESTLA's unit cell.

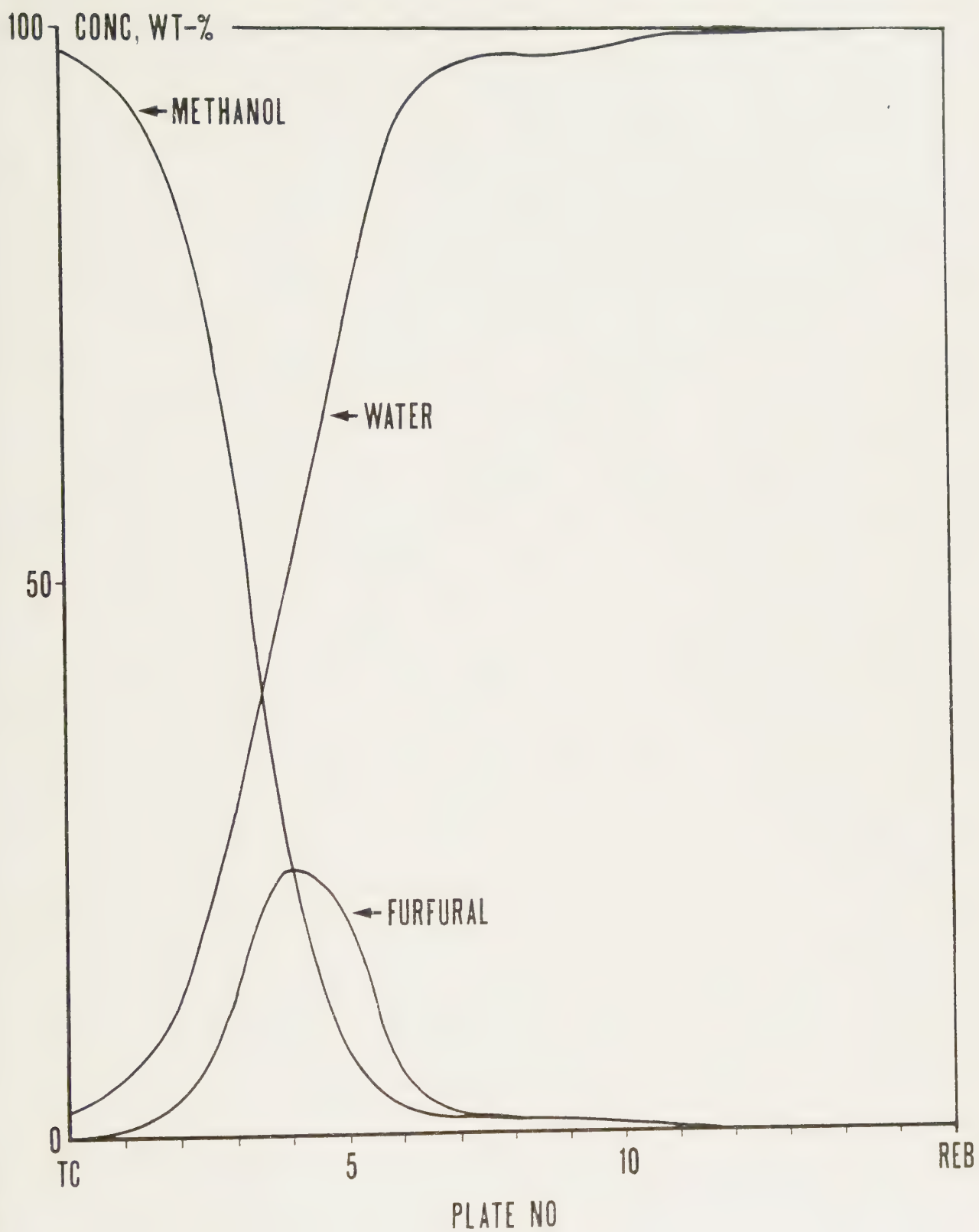


Figure 4. Concentration profiles computed by DESTLA for the methanol column.

SIMULATION AND DESIGN OF DISTILLATION
UNITS FOR TREATMENT OF SULFITE PULPING
CONDENSATES TO RECOVER METHANOL AND
FURFURAL

PART II: APPLICABILITY OF MULTIPLE-
EFFECT DISTILLATION USING
LIVE STEAM

GHARIB ALY AND GUIDO ZACCHI

DEPARTMENT OF CHEMICAL ENGINEERING
LUND INSTITUTE OF TECHNOLOGY
LUND
SWEDEN

SUMMARY

A distillation unit has been designed for a capacity of 73 t/h of condensate and for at least 90 % recovery of the contaminating organics. This unit consists of three columns: a primary stripper to remove volatile organics and two upgrading columns to purify the methanol and furfural byproducts.

Three different energy-saving alternatives for satisfying the energy requirements have been studied: utilisation of secondary steam from the evaporation plant, and application of the principle of multi-effect distillation in one-stripper and in two-stripper configurations.

Investment cost needed in all alternatives amounts to 5.5-6.0 MCr while operating cost varies between 0.8-3.1 MCr. The first design alternative has a payoff period of 2.3 years while the two multi-effect distillation alternatives have a payoff period of about 3 years.

INTRODUCTION

The purpose of the present work was to investigate the potential of using distillation to treat sulfite pulping condensates, from both cooking and evaporation units, for the recovery of economic byproducts, essentially methanol and furfural. Rather than examining just the distillation process as such, the primary emphasis has been focused on economising the energy needs for a unit operation of this type. For this purpose three possible alternatives have been investigated during the course of the present work. The first alternative would use secondary steam already available in the plant by incorporating the primary stripper in the evaporation unit. The use of live steam and application of the principle of multi-effect distillation were investigated in the other two alternatives. The results obtained for the first design alternative were presented in Part I of this work¹. The other two alternatives together with an economic analysis are presented in this paper.

ENERGY-SAVING TECHNIQUES

Distillation towers can take a significant amount of the total energy requirement of a chemical process plant. Fuel shortages and steadily increasing energy prices are now making energy-saving techniques more economically feasible. There are a number of useful techniques worth examining which have been known for quite some time and a brief literature survey²⁻⁸ will yield several practical options and guidelines for their applications. Intermediate heat input and heat removal, vapor recompression and multi-effect principle are some examples.

A system that combines vapor compression evaporation of black liquor with steam distillation of foul condensates has recently been described by Beder and Madrid⁹. Minimization of stripper energy requirement was achieved through extensive preconcentration of condensate volatiles by preevaporation of black liquor in a vapor compression evaporator. Overall steam requirement was less than half that of a conventional system. At a 15 % steam-to-feed ratio, methanol and BOD removal efficiencies in the distillation column were 98 % and 90 % respectively. The column was 3 m in diameter, contained 18 trays and operated under vacuum. The concentration of methanol in the overhead product was kept at about 15 % by weight to allow it to support its own combustion in the lime kiln.

As far as multi-effect principle is concerned, Tyreus and Luyben⁶ suggested that a single tower with a steam consumption greater than about 13.6 t/h might be replaced by a two-tower system to give higher profitability. This limit was however based on considerably lower energy prices than those prevailing today.

Multi-effect principle and vapor recompression qualify directly for the fractionation problem under consideration. In this paper, the applicability of multi-effect distillation is discussed in detail but the vapor recompression technique is dealt with only from an economic point of view.

APPLICABILITY OF MULTI-EFFECT DISTILLATION

The distillation unit with a primary stripper and two upgrading columns was computed by DESTLA. The simulations were based on the same assumptions and environmental requirements described in Part I of this work¹. Since live steam at 400 kPa will be used instead of secondary evaporation steam, the fourth assumption will thus be relaxed. Similarly, the computation procedure applied is nearly the same as that described in Part I.

The two remaining design alternatives, discussed here, concern the applicability of multi-effect distillation using live steam. One uses a single primary stripper and the other uses two primary strippers operating in parallel.

The one-stripper configuration

In this case the reboiler of the methanol column, column II, and the condenser of the stripper, column I, are combined into a single heat exchanger, REB2, as shown in Figure 1. The stripper receives the entire feed F (about 20.3 kg/s) and separates it into a relatively pure bottom, stream B1, and an overhead product, stream D1, somewhat enriched in methanol and furfural. The feed is preheated, using stream B1, to a temperature which is 10°C below its bubble point. The pressure in the stripper is kept at 225 kPa while that of the methanol column is atmospheric. A liquid side stream SS, containing the highest furfural concentration in the methanol column, is withdrawn and sent to the liquid separation vessel SEP after being subcooled to 30°C. This two-phase mixture is separated into two liquid layers. The water-rich layer AQ is preheated and refluxed to the column while the furfural-rich layer ORG is preheated and pumped to the furfural column, column III, via a storage tank. The furfural column operates at 50 kPa and utilizes live steam S3 at 1 MPa as the energy source in its reboiler.

The results of the computations carried out by DESTLA are summarized in Table 1. It can be observed that 95 % of volatile organics are recovered. The live steam consumption in this configuration amounts to 15.6 % by weight of the condensate stream to be treated.

TABLE 1: COMPONENT FLOW RATES, IN kg/h, FOR ONE-STRIPPER CONFIGURATION

Component	F	<u>Purified Condensates</u>		<u>Byproducts</u>		<u>Energy Streams</u>	
		B1	B2	B3	D2	S1	S3
Methanol	153.3	2.8	0.6	≈0	149.9	--	--
Water	72730	63314	9412	≈0	3.8	11315	60
Furfural	116.8	9.7	0.4	106.5	0.2	--	--

The two-stripper configuration

In this case the feed F is split more or less equally among the two strippers, as can be seen from Figure 2. Feed stream F1 enters the first stripper, column IA, while feed stream F2 enters the second stripper, column IB. Both streams are introduced to the first tray of each column, after being preheated to a temperature which is 10°C below the bubble point, using streams B1A and B1B respectively. Some runs were carried out to investigate the working relationships which affect feed subcooling, such as flow rate and heat content of bottoms leaving the base of each stripper, the size of the heat-transfer area in the feed preheater and product specification. A 10°C subcooling was found to be a suitable alternative. The two strippers, being operated in parallel, perform identical functions; both separate the same feed and yield products with the same specifications. The only difference lies in the pressures of the columns; the first stripper is maintained at 225 kPa while the second stripper operated at atmospheric pressure. With such a configuration, the same amount of feed is treated with almost half the energy input needed for the one-stripper configuration.

The upgrading of the methanol and furfural products resembles that described for the one-stripper configuration except that the methanol and furfural columns are operated at 50 kPa.

Some of the results computed by DESTLA for this configuration are shown in Table 2. Several runs were specifically made to determine the appro-

priate feed split which would give the same stream specifications for the bottoms leaving both strippers. The CPU-time consumed in this case, where both strippers were linked together, was about 3 minutes on a UNIVAC-1108 computer system. As shown in Table 2, 52 % of the feed stream will be pumped to column IA and 48 % to column IB. About 45 % of the condensates will be withdrawn from column IA at 129°C and 42.5 % from column IB at 106°C. The balance will be withdrawn from the methanol column at 87°C.

TABLE 2: COMPONENT FLOW RATES, IN kg/h, FOR TWO-STRIPPER CONFIGURATION

Component	Input streams		Purified Condensates			By-products		Energy Streams	
	F1A	F1B	B1A	B1B	B2	B3	D2	S1	S3
Methanol	79.6	73.7	1.3	1.6	0.3	0	150.1	--	--
Water	37743	34987	32819	30940	8968	0	3.5	5952	60
Furfural	60.6	56.2	4.7	5.0	0.8	106.2	0.1	--	--

As far as the product purities are concerned, both configurations give the same results, i.e. about 98 % of the methanol and more than 91 % of the furfural are recovered. This means that a considerable reduction can be achieved in the COD and BOD₅ of the effluent. The capital cost is somewhat higher in the two-stripper configuration but the live steam consumption is only 8.2 % by weight of the condensate stream to be treated. This will decrease the operating cost for the plant by about 40 %.

As can be seen in Figures 1 and 2, the contaminated feed is first passed into the stripper operating at a relatively high reflux ratio (defined as internal liquid-to-vapor ratio), and the overhead vapor is used to provide the boil-up in the centre-feed methanol column operating at a lower pressure. Since the latter column requires a lower reflux ratio, excess low-pressure vapor can be bled off from the top and used for other purposes. This excess vapor is condensed in a total condenser, TC1, which was designed to preheat the steam reboiler condensate, stream W1. About 4.0 MW is removed in this condenser in the one-stripper configuration and about 0.9 MW in the two-stripper configuration.

DESIGN OF DISTILLATION COLUMNS

Information on vapor-liquid and liquid-liquid equilibria was computed by the computer program EQUIL as described in Part I of this work¹. The computer program DESTLA computed all important data - necessary for sizing the different columns - such as number of theoretical plates, flow rates, compositions, temperatures and heat content of the streams entering or leaving each piece of equipment involved in the distillation unit.

A recently published work¹⁰ offers shortcut techniques, as well as practical advice, for setting the operating conditions, sizing the column, and choosing the internals for distillation columns in general. The Koch Flexitray Design Manual¹¹ provides detailed design procedure for valve trays. These two references were used in the design of the distillation columns involved in this work. The results of the design calculations are given in Table 3.

The furfural column, which has a relatively small diameter and requires only three theoretical stages to purify the furfural stream, was chosen as a packed column with 5/8" metallic Pall rings as packing material. The design data for this column are the same irrespective of the design alternative.

Valve trays are suggested for the stripper and the methanol column. A tray efficiency of 50 % was used in both columns because of the low concentrations prevailing in both the stripper and the stripping section of the methanol column.

TABLE 3: DESIGN DATA FOR PRIMARY STRIPPERS AND UPGRADING COLUMNS

Item	Primary Stripper				Methanol Columns			Furfural Columns	
	Alt. 1	Alt. 2	IA	IB	Alt. 1	Alt. 2	Alt. 3	Alt. alt.	Alt. alt.
Operating pressure, kPa	205	225	225	100	100	100	50	50	
Number of trays	12	48	48	48	30	30	30	Packing	
Feed tray (from top)	4	1	1	1	18	18	18	Top	
Tray efficiency, %	50	50	50	50	50	50	50	HETP = 0.4 m	
Tray spacing, m	0.6	0.6	0.6	0.6	0.5	0.5	0.5	--	
Effective column height, m	7.8	29.4	29.4	29.4	15.5	15.5	15.5	1.2	
Column diameter, m	2.35	1.70	1.00	1.05	1.00	1.20	1.35	0.20	
Reflux ratio	--	--	--	--	26	40	36	--	
Reboiler area, m ²	--	223	118	94	17	55	86	<1	
Condenser area, m ²	--	64	--	24	30	46	61	<1	

ECONOMIC ANALYSIS

Table 4 summarizes capital costs, operating costs, income and payoff periods calculated for the various design alternatives.

TABLE 4: ECONOMIC ANALYSIS FOR THE VARIOUS DESIGN ALTERNATIVES

Item	Alt. 1	Alt. 2	Alt. 3
Total capital cost, kCr	6040	5500	6040
Total operating cost, kCr	790	3090	1830
Total income, kCr	3440	4920	3630
Payoff period, years	2.3	3.0	3.4

Capital costs

There are several types of economic estimates useful for evaluating capital costs of chemical plants. Depending on the type of estimate and the inherent reliability of the cost data, the accuracy may change from a probable 25 % for a factored approach, based on reasonable knowledge of flowsheet and major equipment, to a 3 % for a detailed estimate based on complete drawings and contractor specifications. The former approach is considered in this work.

Some recently published papers^{12,13} provide useful shortcut methods for estimating major chemical process equipments. In addition, information obtainable from some leading Swedish manufacturers gives more definite cost estimates. Estimates of equipment cost in this work were mainly based on manufacturers' information complemented with additional factors extracted from the shortcut methods. As the material of construction, SIS 2343 stainless steel was chosen for all the equipments involved in the distillation plant.

Operating costs

Based on an operating time of 8000 h/a and an average cost of 30 Cr/t of steam, the live steam cost dominates the operating costs. The first design alternative has the lowest steam cost since the stripper in this case utilizes secondary steam from the evaporation plant. It should be noted however that the steam cost in this alternative is based on an evaporation unit operated in a 6-effect mode. Labor requirement was estimated as 2 man-h/shift since distillation plants are usually designed with a high level of automation.

Income

The sale value of the furfural product is an important parameter in the economic analysis. A sale price of 3500 Cr/t was set up in Table 4 and the results of a sensitivity analysis on the furfural price are displayed in Figure 3. As far as the methanol product is concerned, it was assumed that it will be burned within the plant. The energy value for the methanol produced was therefore taken as 250 Cr/t, which is almost half its sale value.

The excess low-pressure vapor which is bled off in the distillation plant can be used to preheat steam reboiler condensate as discussed earlier. It must be pointed out that neither heat energy removed in the other condensers and product coolers nor the energy content of the bottoms (except that used in feed preheating) was considered in the economic analysis. Similarly, the economic value of the BOD reduction achieved by distillation is neglected. In case the condensate will primarily be treated to decrease its BOD content, this indirect income should be calculated as the incremental cost of a biological treatment unit sized to process the BOD removed by the distillation plant.

Investment profitability

The payoff method was used in this preliminary investment analysis. This is an approximate method that takes into account only capital

costs, operating costs and income. It is however simple and gives a rapid indication of the profitability of an investment.

In calculating the payoff period in the first design alternative, an additional 700 kCr (for an excess heat-transfer area of 700 m^2) was added to the total capital cost to compensate for the temperature drop in the stripper, which gives rise to a drop in evaporation capacity as discussed in Part I of this work. The sensitivity analysis shown in Figure 3 indicates that for a payoff period of, for instance, 3 years the sale price of the furfural product, which is taken as 3500 Cr/t in Table 4, becomes 2800, 3500, and 3800 Cr/t respectively for the three design alternatives. A sensitivity analysis made on the impact of the excess energy indicated that both multi-effect alternatives have practically the same payoff period for an energy price of 20-30 Cr/t steam.

Comparison with vapor recompression

The payoff period was calculated for the case in which a one-stripper configuration is rebuilt as a vapor recompression system operating at atmospheric pressure. In this case the overhead vapor will be compressed and used to reboil the stripper. An additional investment of about 800 kCr would be needed but in this alternative the operating costs are decreased by about 2.0 MCr since live steam will be needed only in the upgrading columns. This would give a payoff period of 3.2 years. As can be seen from Table 4 this is quite comparable with both stripper configurations. Apart from some practical aspects, such as high maintenance frequency since the overhead vapor which will be compressed is rich in SO_2 , this alternative is a strong competitor to the multi-effect alternatives.

PRACTICAL ASPECTS

It should be emphasized that in this work the condensate was treated as a ternary system consisting of methanol, water and furfural. The actual plant condensate contains other organic components, such as acetone, acetic acid and cymenes, as well as SO_2 . To investigate the effect of these compounds, a quantity of 400 litres of cooking condensate from the Nymölla mill was fractionated in two pilot-plant batch distillation units. The condensate, containing 0.23 weight % furfural and 0.38 weight % methanol, was concentrated by repeated batch distillation. The methanol fraction obtained was miscoloured and contained some more unidentified volatile organics. The furfural fraction was colourless and had a concentration of about 98 weight %, i.e. the same purity as furfural of synthesis quality. The contaminants were identified as 5-methyl furfural and 2-acetyl furane in equal amounts together with traces of unidentified components. No acetic acid was detected in either fraction and it must consequently have remained in the still residual.

In a continuous distillation unit, the product purities will be slightly different due to the recycling of some streams. The acetic acid present in the feed would probably remain in the bottoms leaving the stripper and the methanol column. Since the methanol fraction will be burned within the mill, its purity is not a critical factor. The furfural quality, on the other hand, should be satisfactory since it is the only saleable product from the treatment plant. To increase the purity of furfural, it could be withdrawn as a side stream above the bottoms, which in this case constitute less volatile polymerable components. As far as SO_2 is concerned, it will be vented off when the overhead vapor leaving the stripper is condensed. It can be collected and used for fresh acid preparation at a concentration of about 90 % by weight.

CONCLUSIONS

It can be concluded that the first design alternative, incorporating the stripper in the evaporation plant, is the most economically feasible alternative. In practice this would decrease the evaporation capacity due to the temperature drop in the stripper, consequently necessitating an increase in the heating area to compensate for this temperature drop. Incorporating the stripper into an existing evaporation plant would probably create a bottleneck in the washing cycle of the first two effects. A complex control design is another disadvantage associated with this alternative. This incorporation however should be considered for a new sulfite pulp mill.

If the excess low-pressure vapor evolved in both multi-effect configurations is used for example to preheat steam reboiler condensate then both configurations are almost equally profitable for the condensate bulk, 73 t/h, considered in this work. If the steam reboiler condensate could be preheated elsewhere in the mill using a cheap secondary energy stream, then the two-stripper configuration has a much lower payoff period compared to that for the one-stripper configuration. As far as vapor recompression is concerned, the economic analysis gave a payoff period comparable with those for the two multi-effect configurations. Being rich in SO_2 , the overhead vapor to be compressed would necessitate a tailor-made compressor system. Moreover a relatively large reboiler area will be required because of the small temperature drop which can be allowed in the system.

The DESTLA computer program for calculation of general multicomponent distillation systems has proved to be a very useful tool for the simulations presented in this work.

REFERENCES

1. Zacchi, G. and Aly, G., Can. J. Chem. Eng., submitted for publication.
2. Robinson, C.S. and Gilliland, E.R., "Elements of Fractional Distillation", 4th ed., McGraw-Hill, New York (1950).
3. Pratt, H.R.C., "Countercurrent Separation Processes", Elsevier Publ. Co., Amsterdam (1967).
4. King, C.J., "Separation Processes", McGraw-Hill, New York (1971).
5. Timmers, A.C., "International Symposium on Distillation", Instn. Chem. Engrs., Brighton, England, Sec 5A, 54 (1969).
6. Tyreus, B.D. and Luyben, W.L., Hydrocarbon Processing, 54, 93 (1975).
7. Tyreus, B.D. and Luyben, W.L., Chem. Eng. Progress, 72(9), 59 (1976).
8. Petterson, W.C. and Wells, T.A., Chem. Eng., 84(20), 78 (1977).
9. Beder, H. and Madrid, L., Tappi, 60(9), 94 (1977).
10. Frank, O., Chem. Eng., 84(6), 111 (1977).
11. Koch Flexitray Design Manual, Bulletin 960 (1960).
12. Miller, J.S. and Kapella, W.A., Chem. Eng., 84(8), 129 (1977).
13. Pikulik, A. and Diaz, H.E., Chem. Eng., 84(21), 106 (1977).

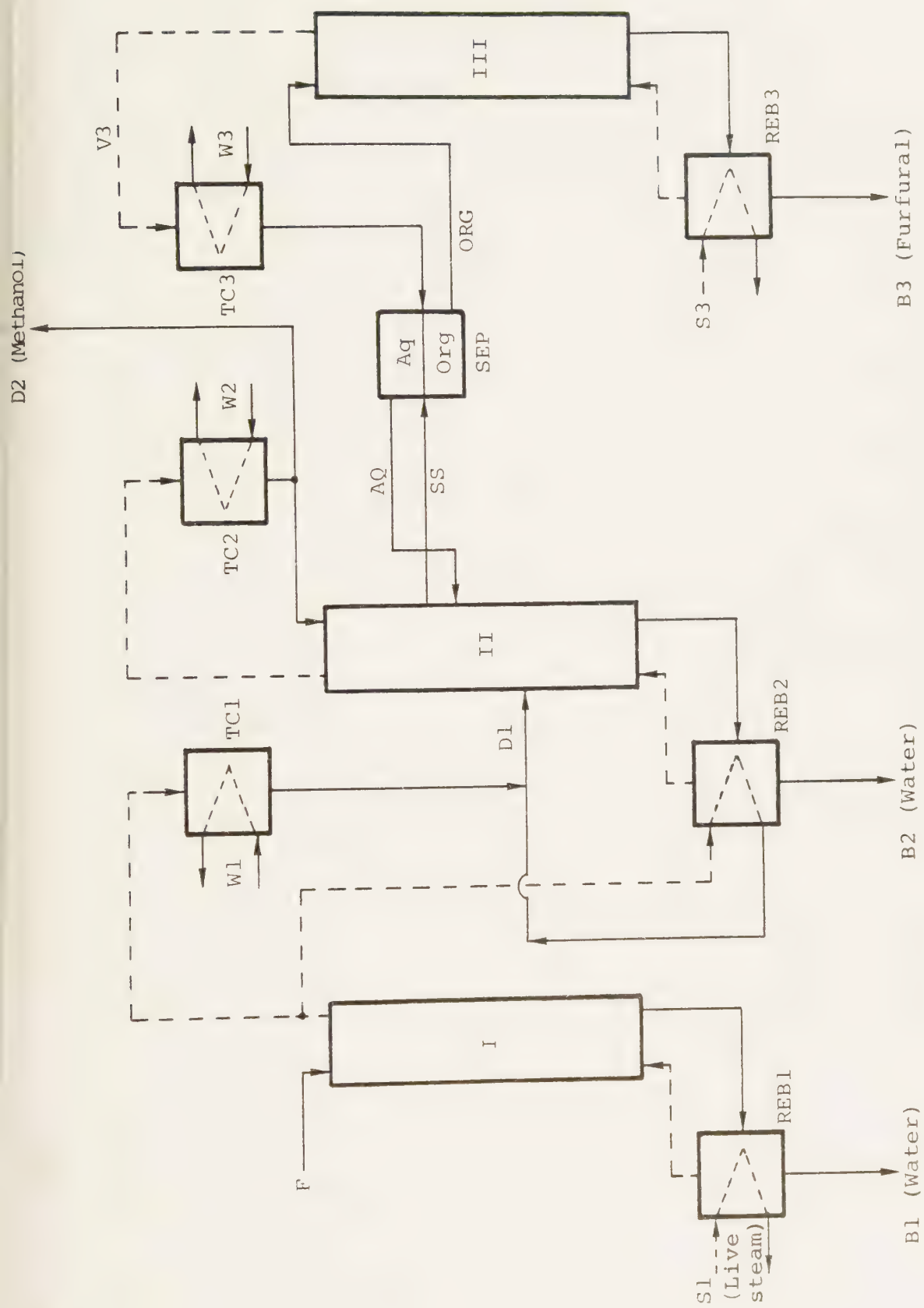


Figure 1. Flow sheet for the one-stripper configuration.

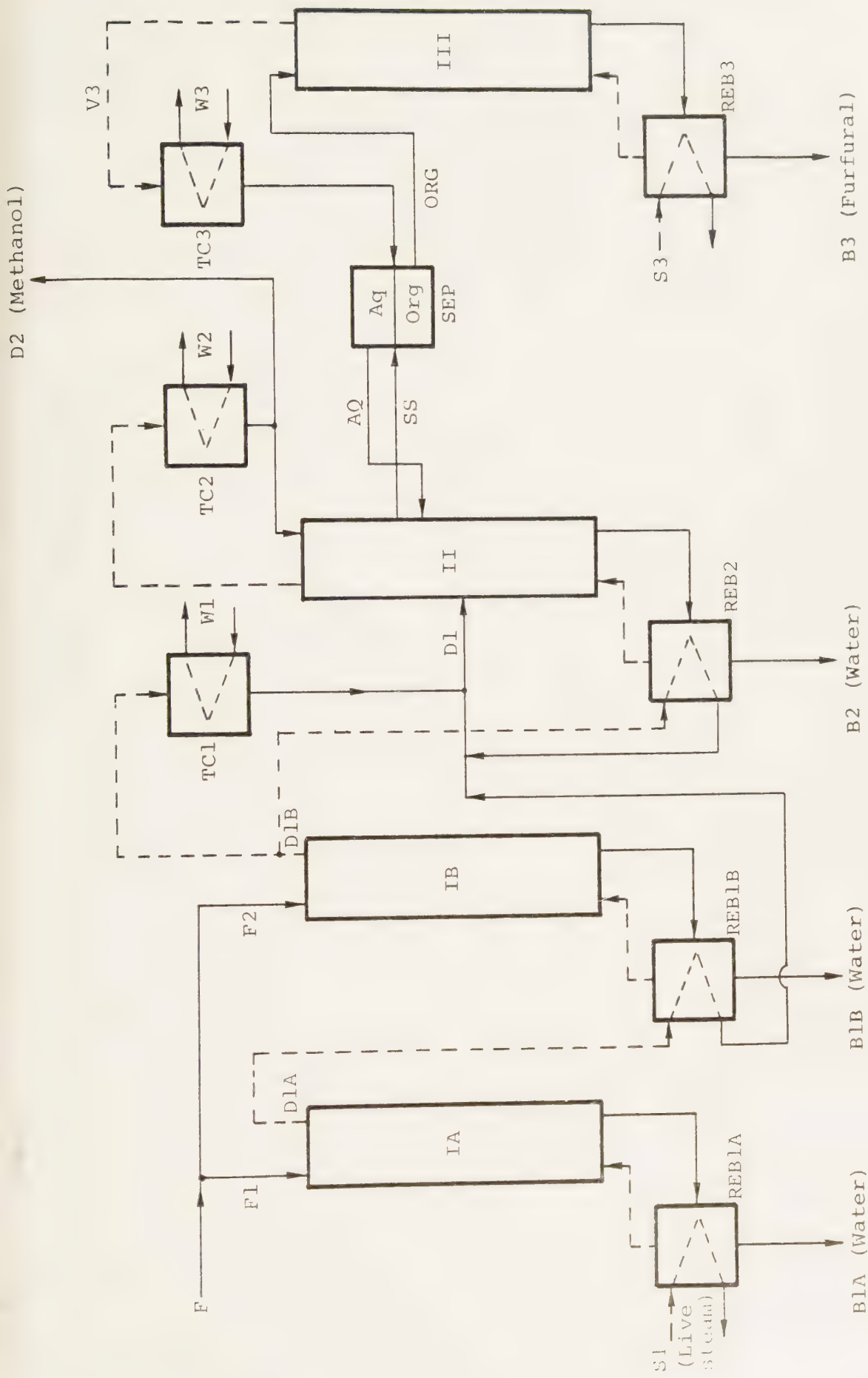


Figure 2. Flow sheet for the two-stripper configuration.

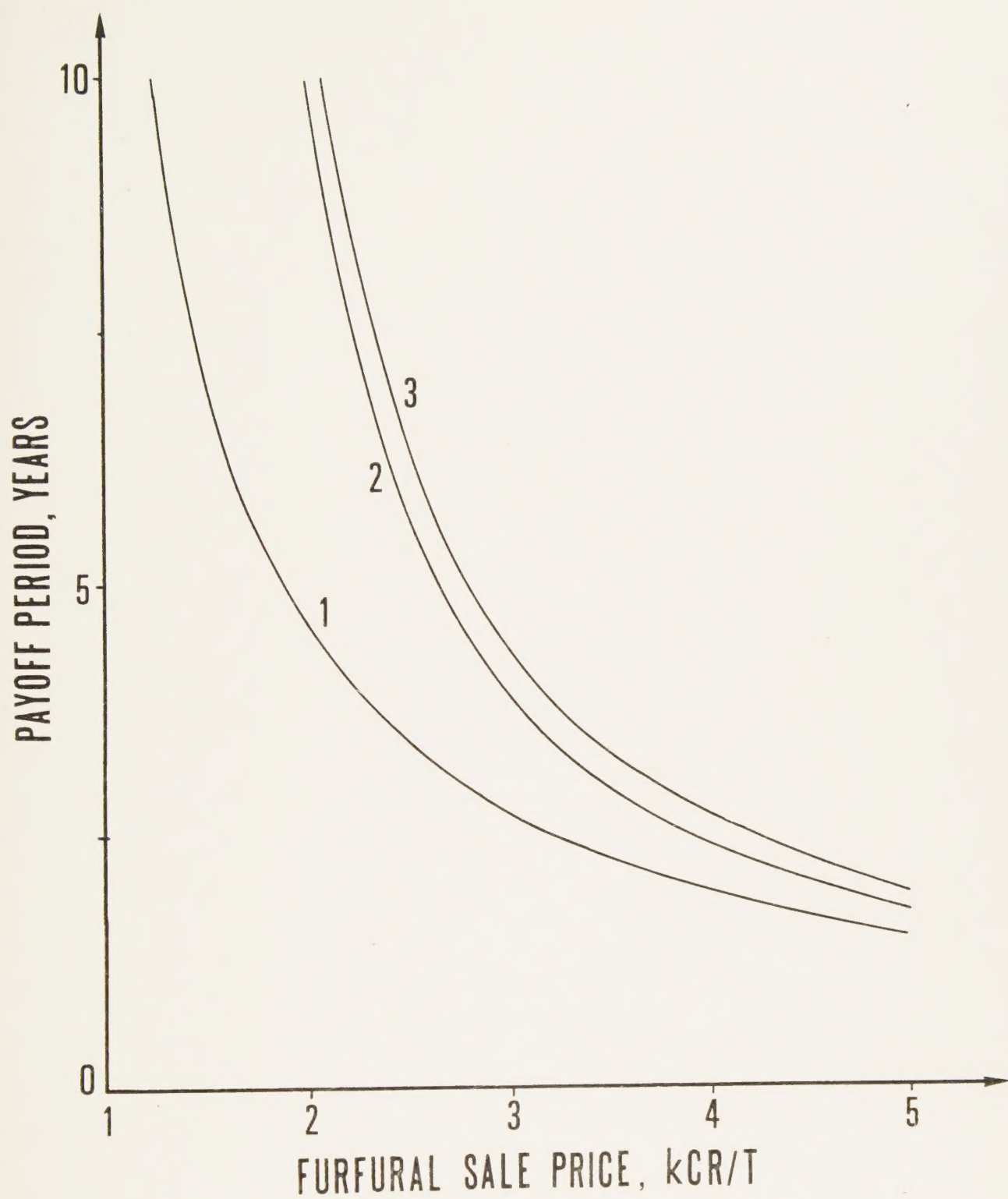


Figure 3. Sensitivity analysis of the furfural sale price.

1. Incorporation with evaporation.
2. One-stripper configuration.
3. Two-stripper configuration.



